SYNTHESIS OF SULFUR- AND NITROGEN-BASED BORANES AND THEIR HYDROBORATION REACTIONS

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By

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DECLARATION

I hereby certify that this research is a result of my own investigation, which has not already been accepted in substance for any degree and is not being submitted in candidature for any other degree.

Signed.....

Siphamandla Wiseman Hadebe

I hereby certify that this statement is correct

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ABSTRACT

This study focused on the synthesis and design of sulfur- and nitrogen-based boranes with a single site available for hydroboration, as well as their interactions with selected alkenes. The reactions were monitored *in situ* with the aid of ^{11}B NMR spectroscopy. The *in situ* monitoring of the reactions clearly indicated the importance of this technique as it was able to unambiguously assign the products of the reactions as well as accurately quantify them.

Initial attempts to synthesise bis(benzylthio)borane showed the formation of benzylthioborane the reaction of BH_3:SMe_2 with benzyl mercaptan. This study has shown that benzylthioborane was converted to tris(benzylthio)borane upon heating at 40 °C. Polymeric alkylthioboranes were also obtained from the reaction of ethyl and isopropyl mercaptans with BH_3:SMe_2. 1,3,2-dithiaborolane was synthesized in good yield (71%) from BH_3:SMe_2 and 1,2-ethanedithiol; this reaction also displayed the formation of the disproportionation product 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane). Yields of product and the disproportionation product fluctuated with temperature and stoichiometry. A reliable synthetic technique for the preparation of 1,3,2-dithiaborolane was developed and. 1,3,2-dithiaborinane was synthesized in 34% yield with the major product being the disproportionation product 2,2′-(propylenedithio)-(1,3,2-dithiaborinane). Benzo-1,3,2-dithiaborolane was synthesized in quantitative yield at 25 °C while 4,7-dichloro-benzo-1,3,2-dithiaborolane was obtained after 7 hour in boiling CH_2Cl_2.

Attempts to synthesise 1,3,2-dioxaborolane, revealed significant disproportionation to 2,2′-(ethylenedioxa)-(1,3,2-dioxaborolane) at 25 °C. Nitrogen-base derivatives, benzo-1,3,2-diazaborolane and 1,3-dimethyl-1,3,2-diazaborolane were synthesized in excellent yields (80 – 95%) from 1,2-diaminobenzene and *N,N'*-dimethyl-1,2-diaminoethane with BH_3:SMe_2 respectively, in boiling CH_2Cl_2 or THF. No disproportionation products were observed spectroscopically. A preliminary study of the factors which influence the

formation of the disproportionation products was conducted using Spartan® '04 V1.0.1, which have allowed for the rationalisation of these results.

A concentration dependence study of the hydroboration of 1-octene with 1,3,2-dithiaborolane at 25 °C afforded a second order rate constant (k_2) of $(1.548 \pm 0.009) \times 10^{-4}$ $M^{-1}s^{-1}$. For hydroboration of 1-octene with 1,3,2-dithiaborinane, the k_2 was found to be $(1,652 \pm 0.013) \times 10^{-4}$ $M^{-1}s^{-1}$. This revealed that the sulfur- based boranes i.e. 1,3,2-dithiaborolane and 1,3,2-dithiaborinane, hydroborated 1-octene significantly slower than $HBBr_2$:SMe_2 complexes and H_2BBr:SMe_2 complexes.[117]

Temperature dependence studies were also conducted for the hydroboration of 1-octene with 1,3,2-dithiaborolane, which displayed the entropy of formation of octyl-1,3,2-dithiaborolane from the depletion of 1,3,2-dithiaborolane to be (-174.45 ± 11.49) JK^{-1} mol^{-1}, and the enthalpy of formation of octyl-1,3,2-dithiaborolane to be (-41.30 ± 3.45) $kJmol^{-1}$. For the hydroboration of 1-octene with 1,3,2-dithiaborinane, the entropy of formation of octyl-1,3,2-dithiaborinane was found to be (-208.49 ± 11.52) $JK^{-1}mol^{-1}$ and the enthalpy of formation of octyl-1,3,2-dithiaborinane from depletion of 1,3,2-dithiaborinane was found to be (-31.02 ± 3.46) $kJmol^{-1}$. The large and negative entropy values obtained for both reactions supported an associative mechanism.

Aromatic derivatives oxygen-, sulfur-, and nitrogen-based borolanes exhibited the expected reactivity trend towards olefins. The reactivity of these reagents was found to decrease with increasing magnitude of back donation between the hetero and the boron atoms as follows: benzo-1,3,2-dioxaborolane > benzo-1,3,2-dithiaborolane >> benzo-1,3,2-diazaborolane.

Due to the diminished reactivity of the nitrogen containing borolanes the use of a catalytic systems was employed in order to achieve the desired hydroboration with the alkene. $Cp_2Ti(CH_3)_2$ catalyzed addition of either benzo-1,3,2-dithiaborolane or benzo-1,3,2-diazaborolane to 1-octene did not form desired octylboronate esters, whereas $RhCl(PPh_3)_3$ complex catalysed the addition of benzo-1,3,2-dithiaborolane to 1-and 4-

octene at 25 °C to form desired octylboronate esters in *ca.* 60% yields. No isomeric alcohols were formed from the $RhCl(PPh_3)_3$ catalyzed addition of benzo-1,3,2-dithiaborolane to *trans*-4-octene. Surprisingly, the catalysed addition of benzo-1,3,2-diazaborolane, pinacolborane, and 1,3-dimethyl-1,3,2-diazaborolane to *trans*-4-octene was not successful and is attributed to steric hindrance. However, addition of pinacolborane and benzo-1,3,2-diazaborolane to 1-octene was successfully catalysed by $RhCl(PPh_3)_3$ yielding octyl-pinacol-boronate ester (79%) and the novel octyl-benzo-1,3,2-diazaborolane (70%) respectively.

Chapter 1.

Introduction

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Chapter 2.

Chapter 3.

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- *Ngibonga uMvelinqangi ngakhokonke angenzelekona, Ngiyanibonga nani bako-Bhungane.*

ABBREVIATIONS

B	Boron
BH_3:SMe_2	Borane-dimethyl sulfide complex
CH_2Cl_2	Dichloromethane
Cp	Cyclopentadiene
DG	Diglyme
DFT	Density Functional Theory
d	Doublet
GC	Gas Chromatography
EE	Ethyl ether
H	Hydrogen
HBcat	Catecholborane
HOMO	Highest Occupied Molecular Orbital
J	coupling constant
k_{obs}	Observed rate constant
LAO	Linear Alpha Olefin
LUMO	Lowest Unoccupied Molecular Orbital
m	Multiplet
MS	Mass Spectrometry
N	Nitrogen
NMR	Nuclear Magnetic Resonance
O	Oxygen
PPh_3	Triphenyl phosiphine
S	Sulfur
SMe_2	Dimethyl sulphide
s	Singlet
t	Triplet

1. INTRODUCTION

1.1 Importance of Linear α-olefins

Linear α-olefins are defined as straight chain hydrocarbons containing a double bond at the terminal or α-position. Alpha-olefins are commercially more valuable than the internal olefins; hence there is focused interest towards the production of these compounds. Their chain lengths vary from C_4 (1-butene) to C_{30+}.[1] About 33% of α-olefins are used in the polymer industry as polyethylene comonomers; 22% are used in detergent alcohols; 21% in synthetic lubricants and lube oil additives including polyalpha-olefins (PAOs); 10% in plasticizer alcohols; 3% in alkyldimethylamine and dialkylmethylamines; 2% are used in surfactants including linear α-olefin sulfonates and linear alkylbenzene; 2% in fatty acids and 7% in miscellaneous uses, including the production of mercaptans and alkenylsuccinic anhydrides (ASA).[2]

A new study by C.A. Houston & Associates, Inc.[3] on the world market for α-olefins revealed that the consumption of LAOs (linear α-olefins) in direct end uses totalled 2.5 million tons in 2000 and is forecast to grow at an average rate of 6.6% per year to 2010. The study also indicated that the capacity of α-olefins has increased from 2.4 million tons/year in 1997 to 3.2 million tons/year by year-end 2001, and could reach 4.2 million tons/year by 2005, including both confirmed and potential new plants and expansions.[3]

C.A. Houston & Associates, Inc.[3] also reported that the α-olefins market is facing a complex array of developments, including major new plants and expansions coming on stream in the 2000 - 2004 time frame. Currently, seven companies manufacture a range of α-olefins *via* the most important method for LAO production, that is, ethylene oligomerization and one company produces specific chain lengths from coal-derived synthesis gas.[3]

CpChem's new plant started operating in 2000 in Texas;[2,3] BP brought up a new plant on stream in Canada in 2001; and Shell's new £700 million plant was also brought on

stream in Louisiana in early 2002. There are also other new plants which are under consideration for the 2003 – 2005 time frame and these will be located in the Middle East, Asia and Africa.[3] It is also reported that other additional plants are under consideration, these include new 1-hexene, 1-octene and multipurpose unit planned by Sasol; a joint venture plant proposed by Idemitsu and Formosa Plastics; and a Chevron Phillips new world-scale plant.

This study[3] also showed that by 2004 all the producers will have added capacity and two new producers are expected to be fully operational, the first producer is SABIC which will be manufacturing a full range of α-olefins, and the second one is Q-Chem manufacturing 1-hexene. Both these companies produce *via* ethylene oligomerization.[3]

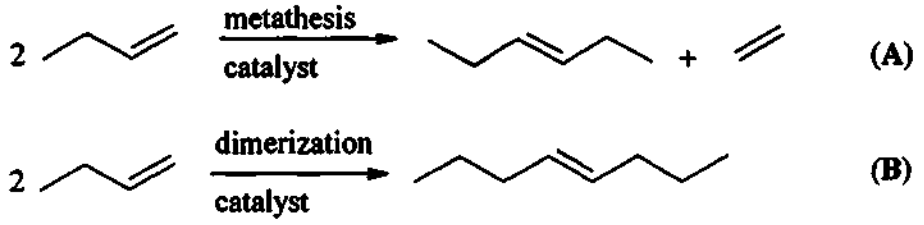
In South Africa, Sasol recovers both odd and even numbered α-olefins ranging from C_5 to C_8 from raw petrol streams produced in the Fischer-Tropsch reaction. Sasol is the sole commercial producer of 1-pentene in the world.[1]

Most of the linear α-olefin producers rely on the ethylene oligomerization as a synthetic route, other synthetic methods for α-olefin production are not considered to be economical routes for manufacturing α-olefins, these processes involve alcohol dehydration, paraffin wax cracking, and internal olefin isomerization.[1]

1.2 Importance of Isomerization of Internal Alkenes to Sasol

It has been stated in the above section that about seven producers of α-olefins manufacture their product *via* ethylene oligomerization. At Sasol, the situation is very different as there are enormous quantities of internal olefins produced *via* metathesis and /or linear dimerization of 1-butene and 1-pentene. This availability of internal olefin feed stock is the driving force for the development of internal olefin isomerization study.

Grubbs *et al.*,[4] reported that 1-alkene metathesis results in the cleavage of an olefinic carbon-carbon double bond of an alkene to yield the corresponding internal alkene and ethylene after reorganization of the fragments. Sasol has excessive amounts of 1-pentene and 1-butene which undergo metathesis as reported by Grubbs *et al.*, to produce internal isomers, 4-octene and 3-hexene respectively[4] (Scheme 1 A).



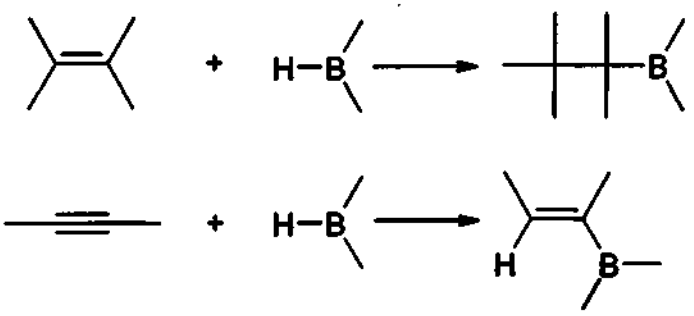
Scheme 1

An alternative method for the synthesis of olefins reported by Ellis *et al.*,[5] is linear dimerization of 1-butene and 1-pentene to form 4-octene and 5-decene respectively (Scheme 1 B). Metathesis and /or dimerization of the short chain 1-alkene followed by isomerization of the internal alkene to the 1-alkene can provide an effective route for the longer chain value added 1-alkene (α-olefin) production.

Brown and Batt[6] showed that internal trialkylboranes can be isomerized and displaced at elevated temperatures to form the corresponding 1-alkenes. The key step in this process is hydroboration yielding the desired alkylborane, this is followed by isomerization and the displacement. These steps are discussed in the subsequent sections.

1.3 Hydroboration

Hydroboration is a reaction that involves a rapid quantitative addition of the boron – hydrogen bond to the carbon – carbon double bonds of alkenes and carbon – carbon triple bond of alkynes[7] (Scheme 2).



Scheme 2

Initial studies in this area by H. C. Brown showed that unsaturated organic compounds are rapidly converted into organoboranes when treated with diborane or diborane precursors in ethereal solvents providing new convenient routes to valuable saturated derivatives such as those shown in Scheme 3.[8,9]

$$9\ RCH{=}CH_2 + 3\ NaBH_4 + AlCl_3 \xrightarrow{DG} 3\ (RCH_2CH_2)_3B + 3\ NaCl + AlH_3$$

$$12\ RCH{=}CH_2 + 3\ NaBH_4 + 4BF_3 \xrightarrow{THF} 4\ (RCH_2CH_2)_3B + 3\ NaBF_4$$

Scheme 3

The use of organozinc[10] or the organomagnesium[11] compounds was shown to be the only practical route to organoboranes, generally the organozinc or the organomagnesium were reacted with the boron halide or ester[12-15] to afford the organoboranes (Scheme 4)

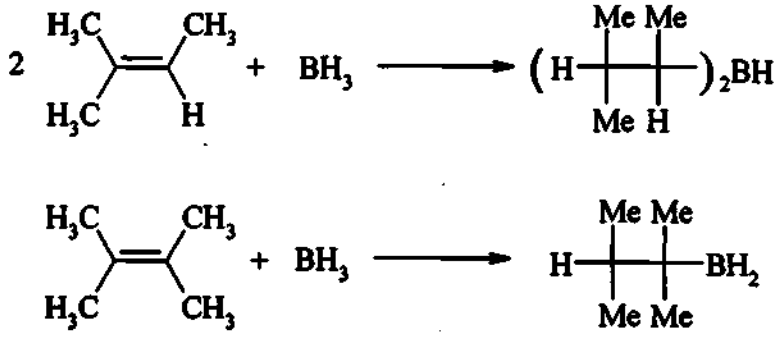
$$3\ Et_2Zn + 2\ BCl_3 \longrightarrow 2\ Et_3B + 3\ ZnCl_2$$

$$3\ PhMgBr + (MeO)_3B \longrightarrow Ph_3B + 3\ MgBr(OMe)$$

Scheme 4

1.3.1 Scope and Stoichiometry

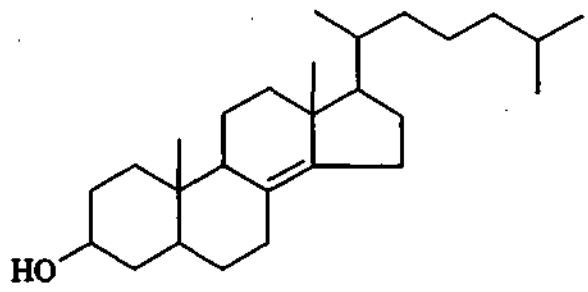
Hydroboration of the majority of simple olefins proceeds simply and rapidly to afford the corresponding organoboranes in high yield. A number of olefins undergo hydroboration reactions to form the corresponding trialkylborane. However, in the case of more hindered alkenes, such as trimethyl ethylene and tetramethyl ethylene, the reaction results in the formation of a dialkylborane or the monoalkylborane[16] (Scheme 5), this has been attributed to the steric hindrance due to the methyl groups around the double bond.



Scheme 5

In cases such as those shown above, it is however possible, to force the reaction to produce the trialkyl substituted molecule such as trisiamylborane or dithexylborane.[17] This is achieved by utilizing relatively concentrated solutions and long reaction times. In the case where the alkyl moieties are relatively stable, higher temperatures have been shown to be necessary to drive the reaction to completion.[17]

In the case of very bulky structures with a double bond deeply buried within the structure such as 5-α-cholest-8(14)-en-3-β-ol (Figure 1.1), it has been noted that the alkene, not surprisingly, fails to undergo hydroboration.[18]



5-α-cholesto-8(14)-en-β-ol

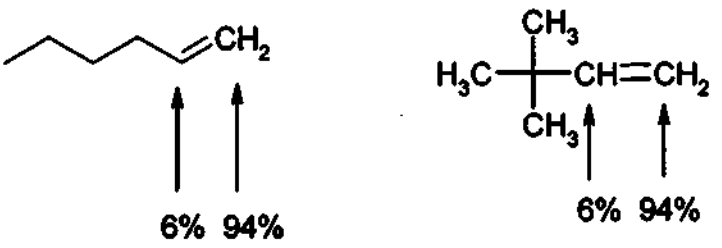
Figure 1.1

The hydroboration reaction involves the anti-Markovnikov addition of B-H across the double bond of the olefin, resulting in the *cis* addition product with the boron atom at the least hindered position of the olefinic double bond. This will be covered in more detail in the following sections (section 1.3.2).

1.3.2 Regioselectivity

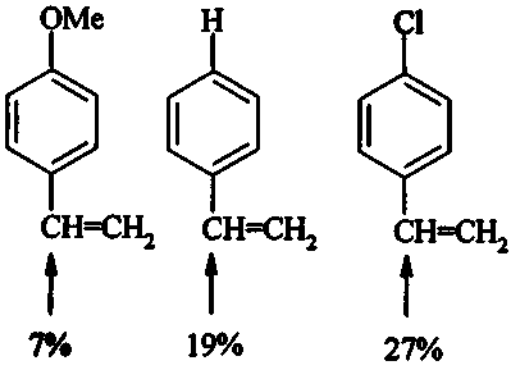
Brown and Zweifel[19] showed that for simple 1-alkenes such as 1-hexene, the hydroboration reaction results in the placement of 94% of the boron atom on the terminal position and only 6% at the 2-position. This distribution is not affected significantly by branching of the alkyl group.[19] (Scheme 6)[π]

[π] BH_3:THF was used as the hydroborating agent in the hydroboration reactions shown in schemes 6, 7 and 8. However, these schemes only show the percentage distribution of the boron atom on the 1- and the 2-positions of the alkene.



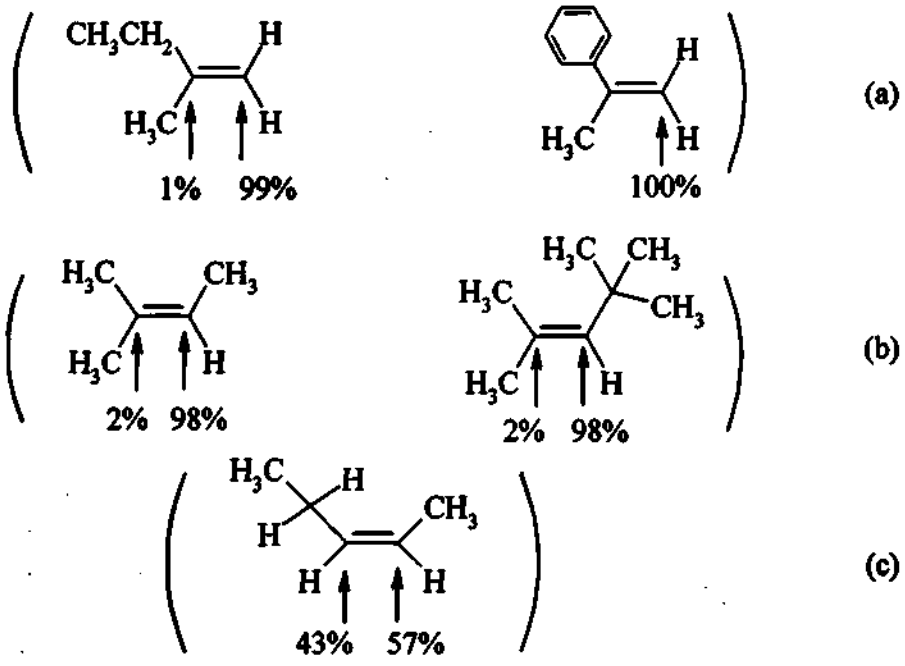
Scheme 6

On the other hand, aryl groups caused increased placement of the boron atom on the non-terminal position.[19] This distribution is significantly changed by substituents on the aromatic ring. Alkoxy groups (EDG) donate electrons into the benzene ring by resonance, leading to decreased placement of the boron at the non-terminal position, while on the other hand halogens (EWG) withdraw electrons inductively from the ring, and this leads to an increase in the placement of the boron atom in the non-terminal position (Scheme 7).



Scheme 7

It has been shown that an alkyl substituent present on the 2-position of the alkene enhances attachment of the boron atom to the terminal position as a result of steric hindrance (Scheme 8a).[19] In the case of internal olefins, a similar preference for the less substituted position is exhibited (Scheme 8b).[19] There is discrimination between the two positions of an internal alkene containing alkyl substituents of different steric requirements (Scheme 8c).



Scheme 8

1.3.3 Mechanism of Hydroboration

Most of the early literature appears to support a mechanism that proceeds *via* a four-centre transition state complex, and the direction of addition is controlled primarily by the polarization of the boron-hydrogen bond.

Jones[20] reported that the proposed four-centre transition state (Figure 1.2 A) has significant symmetry barriers and suggested a three-centre electron-deficient bond implied by π-complex formalism (Figure 1.2 B).

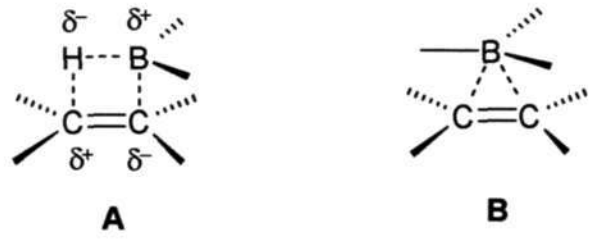
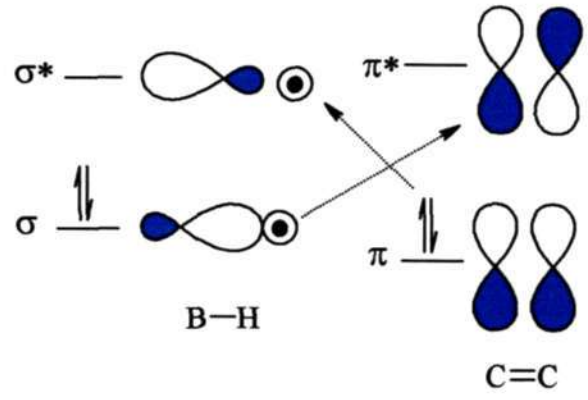


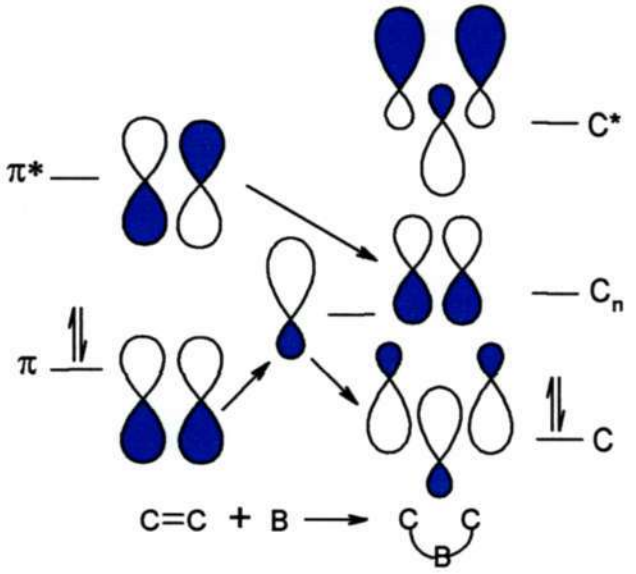
Figure 1.2

The pathway proposed for the 4-center transition state complex as shown in Figure 1.2 **A**, is expected to go through a concerted flow of electrons from the π orbital of the alkene to the σ* orbital of the B-H bond, and from the σ B-H orbital to the π* orbital of the alkene (Scheme 9).



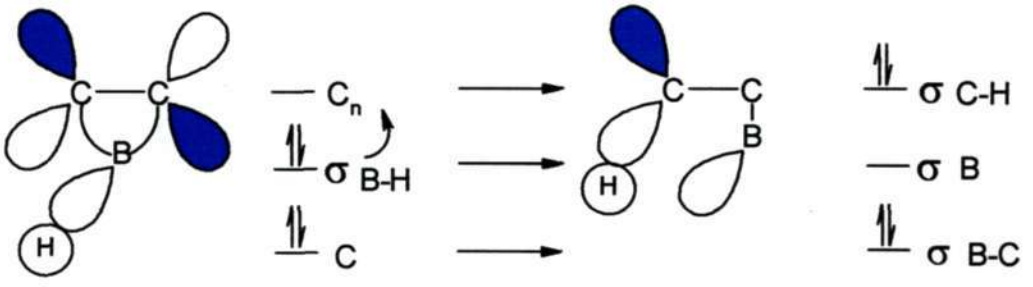
Scheme 9: Symmetry of the orbitals involved in the concerted four-centre reaction of an olefin with a monomeric borane (----indicates a symmetry forbidden process).

This results in a very small net overlap between the pairs of orbitals, thus resulting in a symmetry restriction.[20] The π complex proposed by Jones[20] is shown in Figure 1.2 **B**, here the π complex formation is regarded as the interaction of π electrons from the olefinic double bond with a vacant boron orbital as is the case in the gas-phase reaction of borane with ethylene[21] and this is a symmetry allowed process (Scheme 10).



Scheme 10: Symmetry of the orbitals involved in the reaction of an olefin with borane to form a π complex containing C-B-C three-center bond.

The major arguments against the π complex intermediate (three-center intermediate) are based on the assumption that the π complex must rearrange to a σ complex in later steps of the reaction.[20] Jones[20] showed that the conversion is achieved through the electron flow from the σ system of the moiety involved in the π complex (boron in this case) to the C_n three-centre molecular orbital. A σ bond is formed between carbon and hydrogen as the C_n orbital is occupied, finally the carbon three center bonding orbital of the complex becomes a boron-carbon σ bond (Scheme 11).[20]



Scheme 11: Conversion of C-B-C three center system to two σ bonds

However, Dewar *et al.*[22] reported that the concerted [$_{\pi}2_s$ + $_{\sigma}2_s$] addition of borane to an alkene is not a forbidden reaction because the vacant p-orbital on boron takes part in the process and removes symmetry restrictions. Electrons from the π orbital of an alkene are donated to the empty boron orbital and there is also a back-donation from the B-H bond to the π*-orbital and this process accounts for a concerted addition,[22, 23] this transition state is shown in Figure 1.3 below.

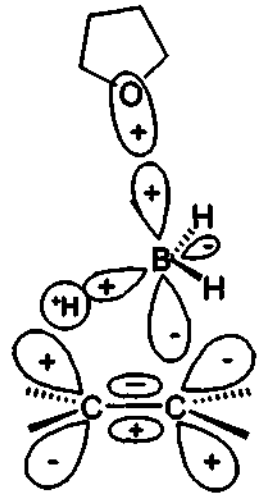


Figure 1.3

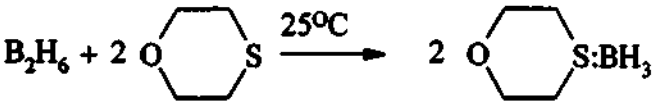
1.4 Hydroborating Agents

1.4.1 Unsubstituted Boranes

Borane-tetrahydrofuran complex (BH_3:THF), is an addition compound derived from dissolving diborane (B_2H_6) in THF.[24 to 27(a)] It is the most stable of the ether complexes, the stability trend observed is BH_3:THF > BH_3:OMe_2 > BH_3:OEt_2.[26] Borane THF complex is the most frequently used hydroborating agent, it reacts very fast with a wide range of alkenes and alkynes at 0 °C and below with predictable regiochemistry.

Borane-dimethyl sulfide complex (BH_3:SMe_2), and its derivatives, show higher stability than corresponding ether complexes. The following stability trend is observed: BH_3:SMe_2 ≥ BH_3:SEt_2 > BH_3:$S(CH_2)_4$,[27(b)] borane-dimethyl sulfide complex is a better hydroborating agent than BH_3:THF due to its stability at room temperature and it can be obtained in concentrations 10 times that of commercial borane-THF solution.[27(b)] Excellent reactivity in many solvents including hydrocarbons has also been observed.[27(b)] It is widely used in hydroboration and in synthesis of a range of hydroborating agents.[28,29]

Borane-1,4-oxathiane complex (Scheme 12) is a stable liquid at room temperature, and is readily synthesized by passing gaseous diborane directly into 1,4-oxathiane at 25 °C to saturation.[30] It hydroborates significantly faster than BH_3:SMe_2.



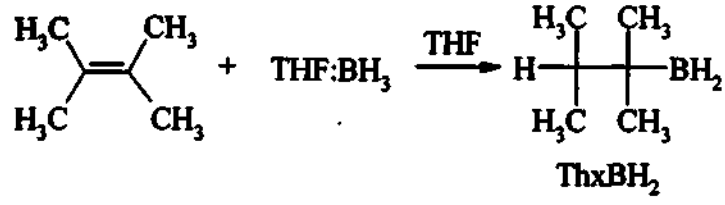
Scheme 12

Borane-amine complexes, a wide range of amine-boranes can be achieved from the reaction of diborane with a desired amine in ethereal solvent.[31] These compounds are very stable liquids or solids and are generally air stable. In addition, they are also soluble in a wide range of solvents, including water. The reactivity of these compounds can be modified by changing the structure of the amine molecule.[31]

1.4.2 Alkylboranes as hydroborating agents

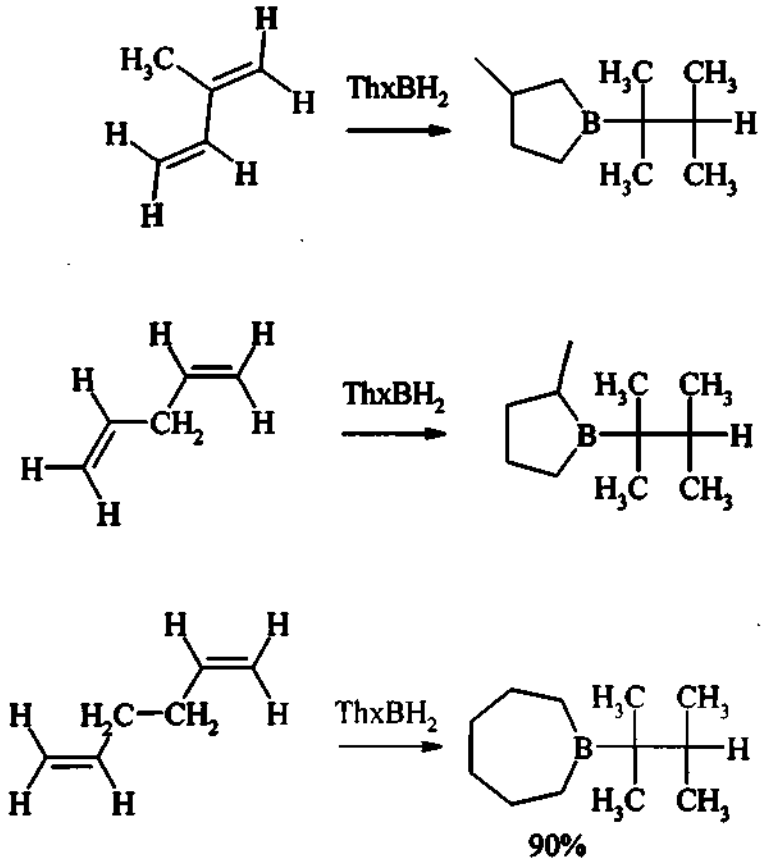
1.4.2.1 Thexylborane

The majority of alkenes undergo hydroboration to form a trialkylborane as the predominant product. However, the hydroboration of certain alkenes can be controlled to yield partially alkylated derivatives. For example, the hydroboration of 2,3-dimethyl-2-butene yields a monoalkylborane compound known as thexylborane[32] (Scheme 13).



Scheme 13

Thexylborane is the most readily available of the monoalkyboranes and has shown to be valuable for the cyclic hydroboration of dienes and numerous other uses.[33] It has also proven to be valuable in achieving the union of two different alkenes to boron and simplified the synthesis of cyclic derivatives (Scheme 14).[33]

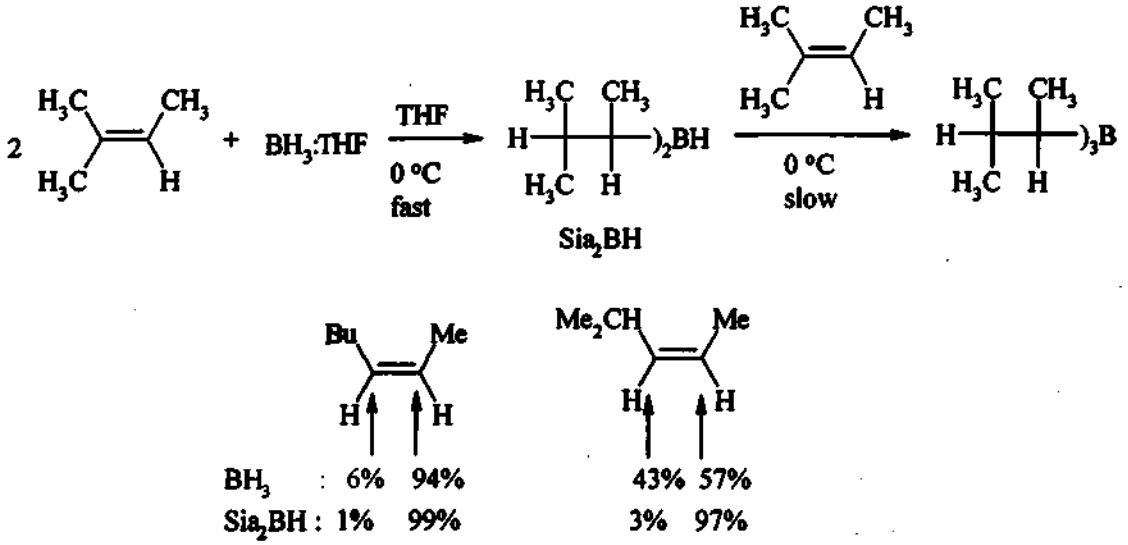


Scheme 14

Thexylborane exists as a monomer in THF solutions due to the large steric interactions exerted by the thexyl group.[17,34] In contrast to diborane, which forms polymeric organoboranes, thexylborane yields β-thexylboraheterocycles in very good yields (Scheme 14).[35-37]

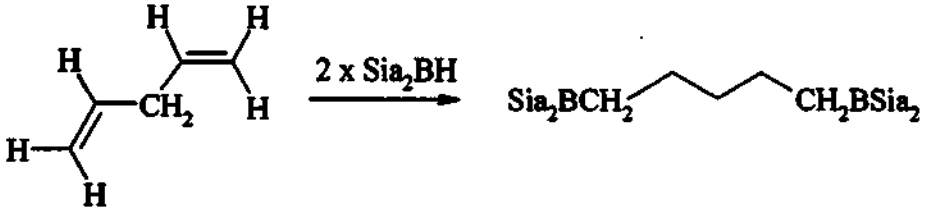
1.4.2.2 Disiamylborane

The hydroboration of 2-methyl-2-butene can be controlled to achieve the synthesis of a dialkylborane called disiamylborane (Sia_2BH) (Scheme 15)



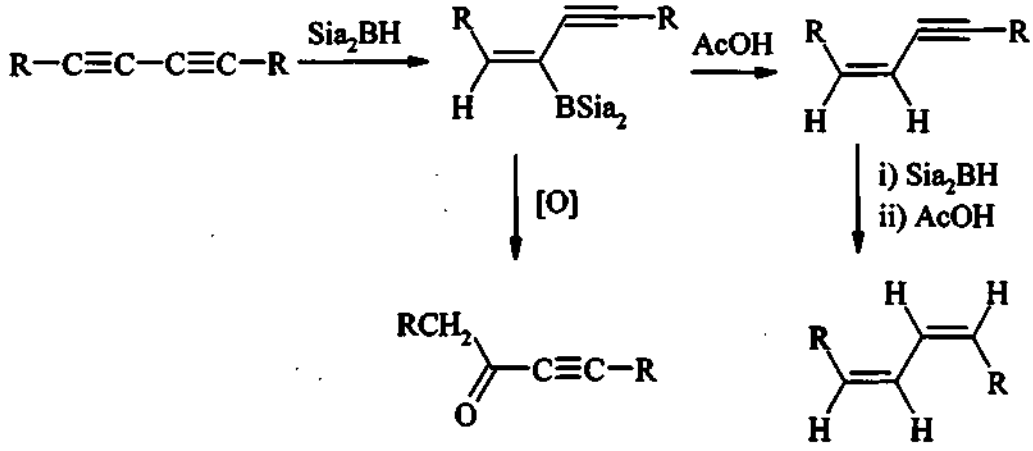
Scheme 15

The above observations (Scheme 15) showed that Sia_2BH possesses enhanced selectivity over that of borane.[38] Sia_2BH exhibits the desired stereoselectivity for the less hindered position of a double bond. This monofunctional reagent is highly sensitive to the structure of the olefin, as a result terminal olefins such as 1-hexene and 2-methyl-1-pentene are more rapidly hydroborated than internal olefins. The advantage of this reagent is derived from its monofunctional nature that avoids the difficulty of accomplishing the dihydroboration of dienes.[39] (Scheme 16)



Scheme 16

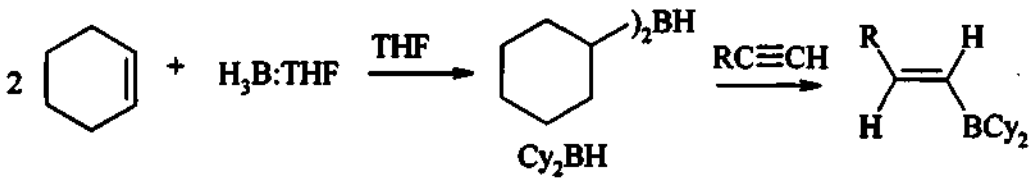
The much higher reactivity of Sia_2BH towards alkynes than alkenes has proved to be useful in the synthesis of (Z,Z)-conjugated and propargylic ketones from the same precursor (Scheme 17).[40] The high steric requirement of Sia_2BH minimizes further reactions with alkenylborane even in the presence of excess reagent.



Scheme 17

1.4.2.3 Dicyclohexylborane

This hydroborating agent is readily produced from the controlled hydroboration of cyclohexene with borane tetrahydrofuran complex. It is advantageous to use this reagent on occasions where less hindered moieties are desired (Scheme 18).[41]

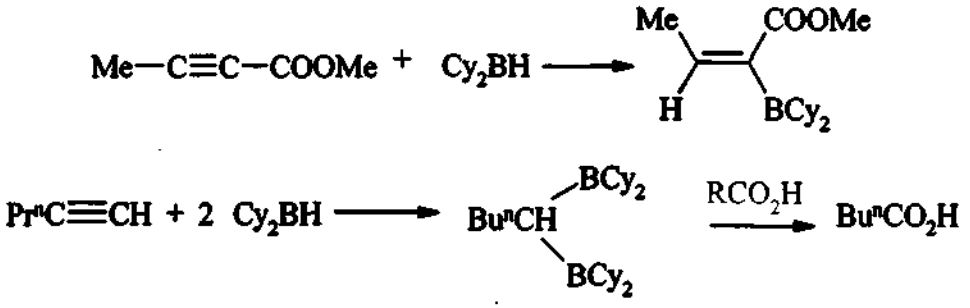


Scheme 18

Hydroboration reactions of dicyclohexylborane (Cy_2BH) parallel those of disiamylborane,[42] if Cy_2BH is used instead of disiamylborane, better yields are achieved and product isolation is also facilitated. Cy_2BH is superior to disiamylborane in applications such as hydroboration of alkynes and thermal isomerization of organoboranes. Disiamylborane shows low thermal stability, this results in the migration of the boron atom (within the reagent) to the terminal position upon heating. This

disadvantage prevents Sia_2BH from being used in reactions requiring high temperatures, while on the other hand Cy_2BH circumvents this difficulty.

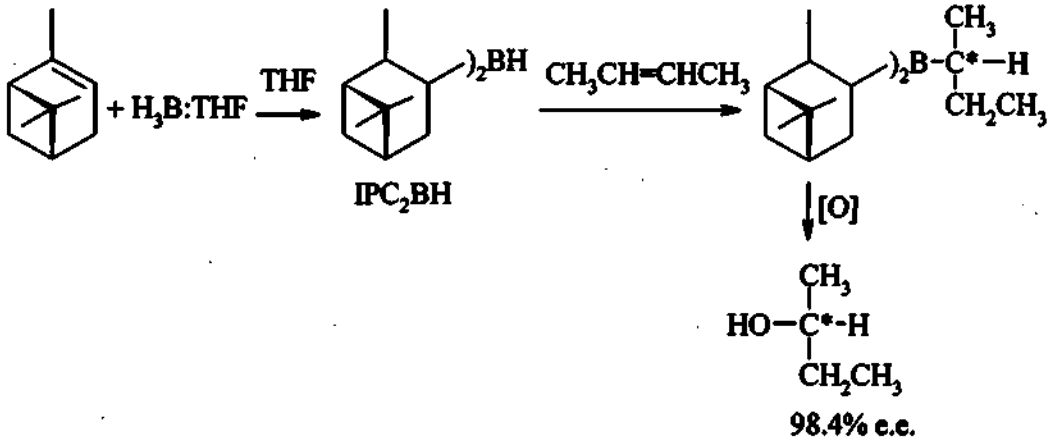
Cy_2BH permits more potential dihydroboration of alkynes due to its reduced steric requirements than those of Sia_2BH.[43] Consequently, hydroboration of terminal alkynes can be controlled to yield either vinylboranes[44] or *gem*-dibora derivatives (Scheme 19)



Scheme 19

1.4.2.4 Diisopinocampheylborane

The controlled hydroboration of α-pinene proceeds readily to the formation of an optically active hydroborating agent known as diisopinocampheylborane. This reagent can be afforded in both optically active forms, (+)-and (-) because α -pinene is available from natural sources in both optically active forms. IPC_2BH makes possible asymmetric hydroboration with remarkable asymmetric induction[45] (Scheme 20).

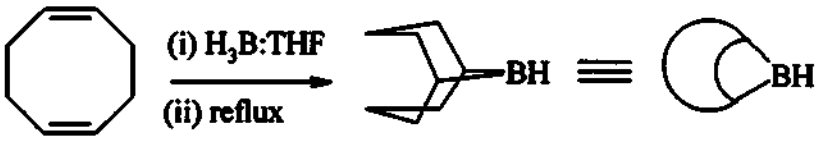


Scheme 20

In Scheme 20, the reaction of *cis*-2-butene with IPC_2BH in its enantiomerically pure form resulted in the formation of an organoborane which, upon oxidation with alkaline hydrogen peroxide, yields (-)-2-butanol, $[\alpha]_D^{20} = -11.8^\circ$ in an enantiomeric excess of > 98.4%.[46]

1.4.2.5 9-borabicyclo[3.3.1]-nonane

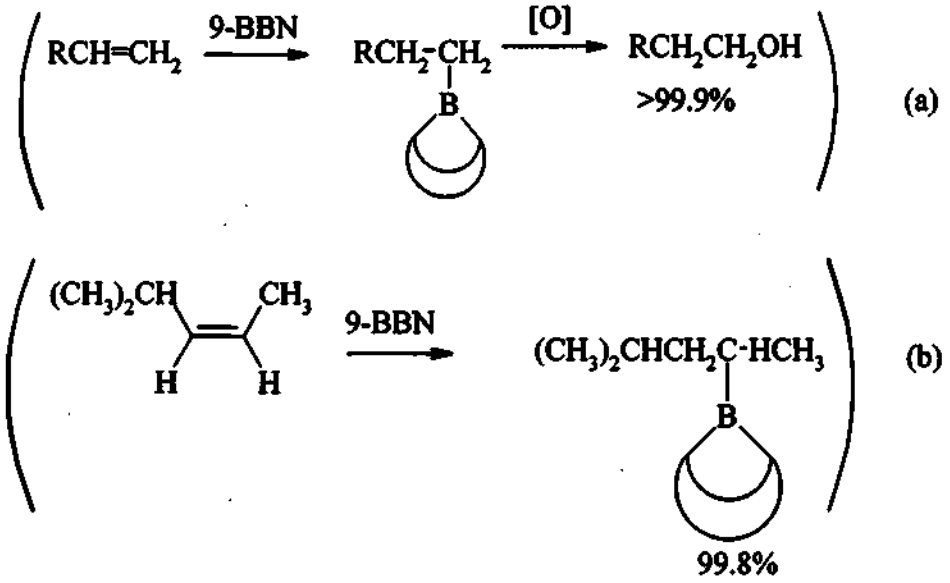
This reagent 9-borabicyclo[3.3.1]nonane, termed 9-BBN for convenience, is obtained from a controlled reaction of 1,5-cyclooctadiene with borane in THF (Scheme 21). It has a remarkable thermal stability. It also exhibits remarkable regioselectivities, even greater than those of disiamylborane.



9-BBN

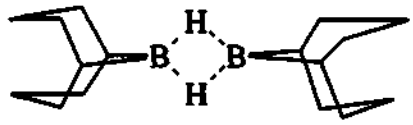
Scheme 21

The hydroboration reaction of this reagent with terminal olefins leads to the placement of the boron atom at the terminal position with a selectivity of at least 99.9% (Scheme 22 a). Interestingly is the regioselectivity exhibited on cis-4-methyl-2-pentene which is essentially exclusive for the secondary carbon (Scheme 22 b).[47]



Scheme 22

It has been shown from the spectral properties[47] and X-ray data[48] that 9-BBN exists as a dimer $(9\text{-BBN})_2$ in the solid state (Scheme 23). It also exists exclusively as a dimer in certain solvents, for example tetrachloromethane, cyclohexane, benzene and diethyl ether.[27(b)] However, an equilibrium is observed between $(9\text{-BBN})_2$ and a solvent complex 9-BBN monomer, if the dimer is dissolved in THF or SMe_2. The monomer has been shown by kinetic studies to be the active hydroborating agent (Scheme 23).[27(b)]



9-BBN dimer

$$(9\text{-BBN})_2 \overset{THF}{\rightleftharpoons} 2\ (9\text{-BBN:THF})$$

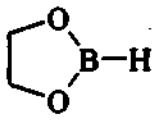
$$9\text{-BBN:THF} + \text{alkene} \xrightarrow{THF} \text{alkyl-9-BBN}$$

Scheme 23

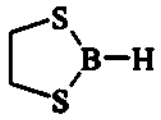
9-BBN shows reduced reactivity towards alkenes than disiamylborane, internal alkenes are hydroborated at 60-80 °C in 1 hour.[27(b)] Temperature elevation is permitted by its thermal stability. This reagent also hydroborates tetrasubstituted double bonds which fail to react with Sia_2BH.[49] 9-BBN has other two applications beside hydroboration: it is used in the reduction of carbonyl groups of α,β-unsaturated aldehydes and ketones with 100% selectivity, yielding allylic alcohols in high yields.[50] Secondly, it forms a complex with pyridine and reduces aldehydes in the presence of ketones.[51]

1.4.3 Heterosubstituted Boranes As Hydroborating Agents

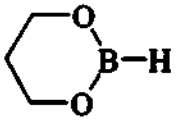
There is a wide range of heterosubstituted boranes, these reagents are defined as borane compounds which are characterized by an oxygen, sulfur, nitrogen and halogen substituents on the boron atom. These compounds include a family of heterosubstituted borolanes (a five membered ring with a single boron atom) and borinanes (a six membered ring with a single boron atom) (Figure 1.4). All these reagents show reduced reactivity if compared to BH_3 or dialkylborane, this is due to the bonding between oxygen or sulfur and boron,[27(b)] which lowers the Lewis acidity of the boron atom.



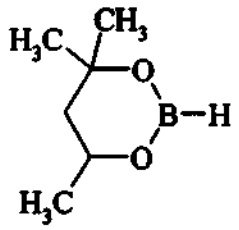
1,3,2-dioxaborolane



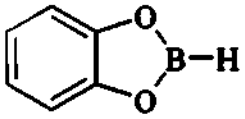
1,3,2-dithiaborolane



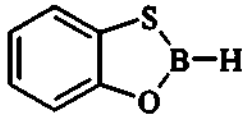
1,3,2-dioxaborinane



4,4,6-trimethyl-1,3,2-dioxaborinane



benzo-1,3,2-dioxaborolane
(catecholborane)

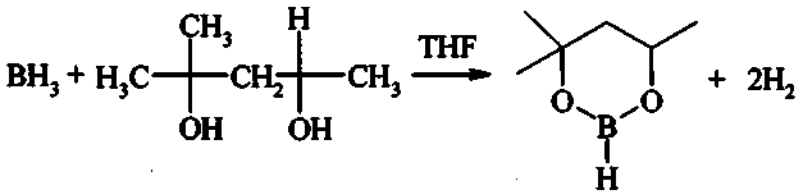


1,3,2-Benzooxathiaborole

Figure 1.4

1.4.3.1 4,4,6-Trimethyl-1,3,2-dioxaborinane

The reaction of glycols and alcohols with borane can be controlled to produce disubstituted boranes (Scheme 24). These derivatives are poor hydroborating agents due to the fact that the oxygen substituents supply the electron density to boron thus greatly decreasing the electrophilic character of the reagent.



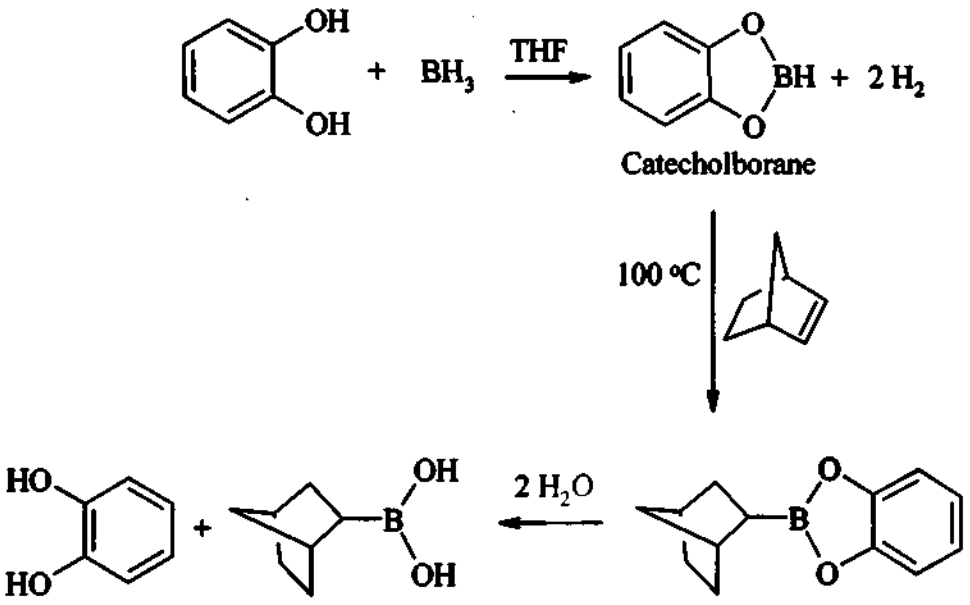
$$BH_3 + 2\,CH_3OH \xrightarrow{THF} (CH_3O)_2BH + 2H_2$$

Scheme 24

1,3,2-Dioxaborinane, 1,3,2-dithiaborolane, and 1,3,2-dioxaborolane (Figure 1.4) undergo disproportionation.[52,53] As a result 1,3,2-dithiaborolane requires stabilization as an amine complex which is liberated by addition of boron trifluoride when used for hydroboration.[53] The two aromatic ring systems, catecholborane and 1,3,2-benzooxathiaborole, are free from such problems due to the conjugation of the aromatic ring with the lone pair of oxygen or sulfur. Very little information is available on 1,3,2-benzooxathiaborole as a hydroborating agent, it has been reported that 1,3,2-benzooxathiaborole hydroborates cyclohexene at 83 °C in 3 hours.[54]

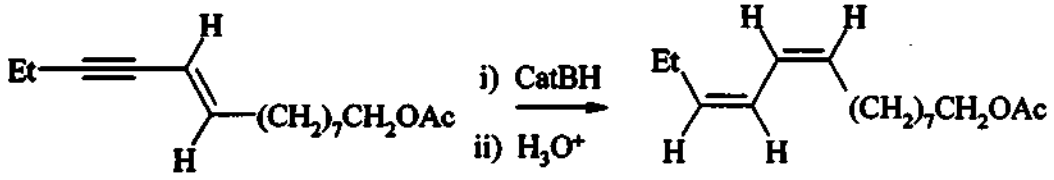
1.4.3.2 Catecholborane

1,2-benzenediol (catechol) undergoes a reaction with borane in THF analogous to that undertaken by glycols, to afford the product benzo-1,3,2-dioxaborolane termed "catecholborane". This reagent is a considerably better hydroborating agent than another alkoxy derivatives. Olefins are readily hydroborated at 100 °C using this reagent (Scheme 25).[55]



Scheme 25

The main advantage of catecholborane derivatives obtained over other dialkylboranes is that they are converted easily into the corresponding boronic acids by hydrolysis (Scheme 25). The disadvantage of this compound is that it has a reduced reactivity in the hydroboration process, alkenes are hydroborated at 100 °C and alkynes at 70 °C. The higher reactivity of alkynes allows for the selective hydroboration of triple bonds in the presence of double bonds (Scheme 26)[56]



Scheme 26

1.4.3.3 Chloroboranes

Borontrichloride reacts readily with diboranes in ethereal solvents to form the corresponding choroborane-etherates. Dichloro- and monochloroboranes are unstable species and they disproportionate to diborane and boron trichloride. The use of ethereal solvents prevents this disproportionation by forming the corresponding ether complexes (Scheme 27).[57]

$$B_2H_6 + 4\ Cl_3B{:}OEt_2 + 2OEt_2 \xrightarrow{\text{ethyl ether}} 6\ Cl_2BH{:}OEt_2$$

$$B_2H_6 + Cl_3B{:}OEt_2 + 2OEt_2 \xrightarrow{\text{ethyl ether}} 3\ ClBH_2{:}OEt_2$$

Scheme 27

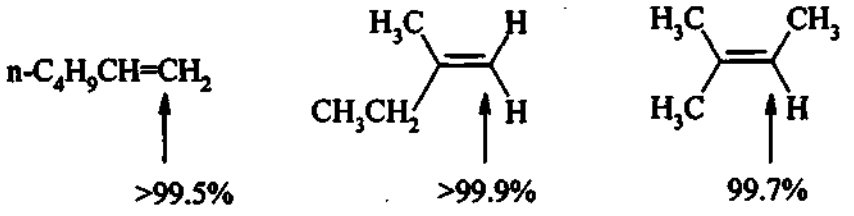
An alternative route to afford the above mentioned complexes is through the reaction of hydrogen chloride with borane-tetrahydrofuran (Scheme 28).[58]

$$H_3B{:}THF + 2\ HCl \xrightarrow{THF} Cl_2BH{:}THF + 2\ H_2$$

$$H_3B{:}THF + HCl \xrightarrow{THF} ClBH_2{:}THF + H_2$$

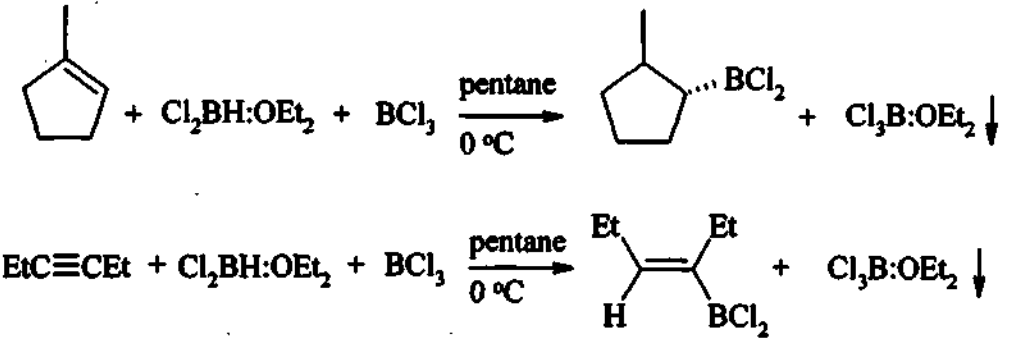
Scheme 28

Monochloroborane-diethyl etherate hydroborates alkenes readily at 0 °C.[59] It exhibits a powerful directive effect in the hydroboration of terminal alkenes (Scheme 29), much greater than that of borane itself, and it is comparable to 9-BBN in many cases.[59]



Scheme 29[8]

Dichloroborane-diethyl etherate is a much less reactive hydroborating agent, it fails to react spontaneously with olefins. This compound hydroborates alkenes and alkynes if one molar equivalent of boron trichloride is added to a mixture of the reagent and the unsaturated organic compound in pentane, this leads to a precipitation of boron trichloride-diethyl etherate and yields a rapid hydroboration process (Scheme 30).[60]



Scheme 30

Unfortunately these reagents are unstable on storage.[27(b)] As a result it is desirable that they be freshly prepared before use. These difficulties can be avoided with the haloborane-dimethyl sulfide adducts (Scheme 31). These chloroboranes behave very similarly to the corresponding etherates.[27(b)]

[8] $ClBH_2$:THF was used in the hydroboration of the three alkenes shown in this scheme, but this scheme mainly emphasize on the directive effect observed.

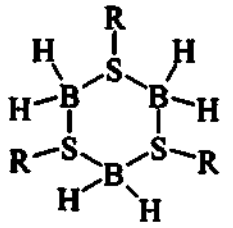
$$H_3B{:}S(CH_3)_2 + 2\ Cl_3B{:}S(CH_3)_2 \longrightarrow 3\ Cl_2BH{:}S(CH_3)_2$$

$$2\ H_3B{:}S(CH_3)_2 + Cl_2B{:}S(CH_3)_2 \longrightarrow 3\ ClBH_2{:}S(CH_3)_2$$

Scheme 31

1.4.3.4 Alkylthioborane Chemistry

The reaction of mercaptans with diborane gives rise to a number of different products depending on the experimental conditions.[61] In the early 1960's Mikhailov and co-workers showed that the reaction of mercaptans with diborane leads to a mixture of mono- and bisalkylthioboranes in proportions that depend on the nature of the thiol.[62] The reaction of 1-propanethiol with diborane afforded a mixture containing 73% of mono(propylthio)borane and 27% of bispropylthioborane. For 1-butanethiol, the product contained 60% of the monosubstituted borane and 40% of the bisalkylthioborane.[62] Monosubstituted boranes were obtained as trimers. Polymeric alkythioboranes were obtained from the reaction of ethyl or butyl mercaptans with diborane in diethyl ether, these polymers convert to trimers (Figure 1.5) upon standing.[63]



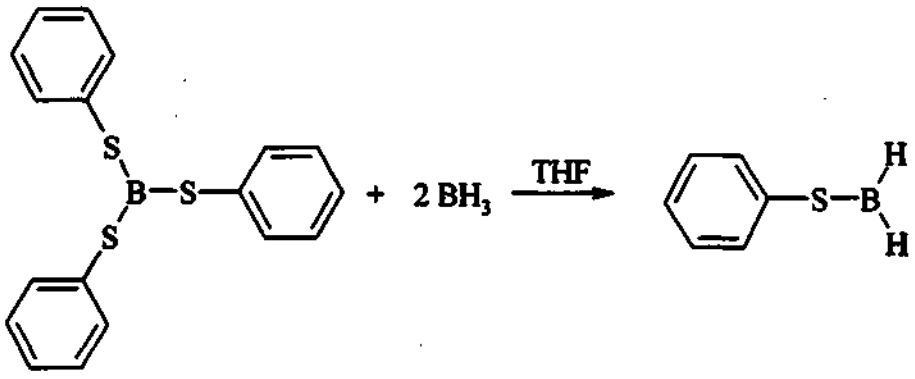
where R = C_2H_5 or C_4H_9

Figure 1.5

Dimeric species of $(BuS)_2BH$ are also obtained from the reaction of butyl mercaptan with diborane.[64, 65] Monomeric phenylthioborane was obtained from the reaction of excess thiophenol with borane in THF or diglyme, during this reaction 1 mole of hydrogen gas was evolved rapidly per mole of borane at 0 or 25 °C.[61]

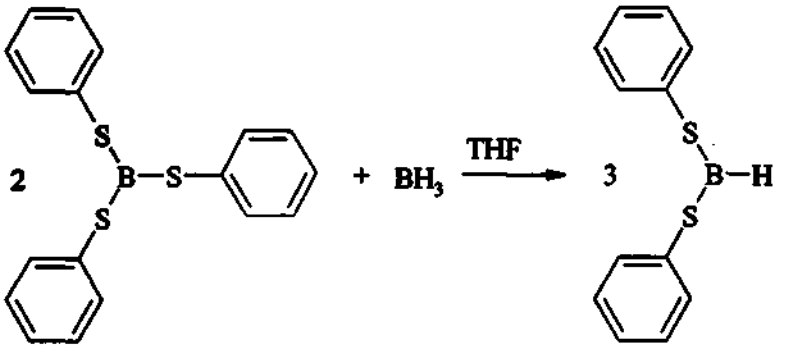
The infrared spectrum of the reaction product from thiophenol and borane in a 1:1 mole ratio showed absorption in the 2420cm^{-1} region characteristic of terminal B-H stretching frequencies.[66] The absence of absorption bands corresponding to bridged hydrogens exclude the presence of polymeric species. The absence of bridged hydrogens was also confirmed by ^{11}B NMR spectroscopy that displayed a triplet at -3.3 ppm relative to BF_3:OEt_2.[61] This is in contrast to benzyl mercaptan with borane in THF which showed only a broad singlet at +14.7 ppm, attributable to polymeric benzylthioborane in which the backbone of the polymer is a sequence of -B(H_2)-SR- units.

The alternative route for the synthesis of phenylthioborane is through the disproportionation of triphenylthioborate (Scheme 32) with borane in THF.[61] Phenylthioborane synthesized by this route is identical in physical and chemical properties with one prepared directly from thiophenol and borane.



Scheme 32

Diphenylthioborane (Scheme 33) can be obtained from the reaction of 2 moles of triphenylthioborate with 1 mole of borane in THF.[66]

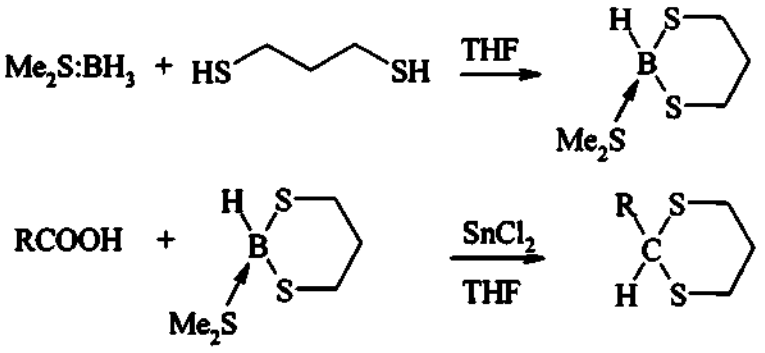


Scheme 33

Phenylborane has been described as being monomeric while all other mono- and dialkylborane exists as dimers. According to Sanderson's calculations,[e] the dimerization of substituted boranes occurs only when the hydrogens have partially negative charge based on electronegativity considerations. Sanderson's calculations reveal that the hydrogen bonded to boron in phenylboranes are partially positive while those in alkylboranes are quite negatively charged. This indicates that phenyl group acts as a powerful electron-withdrawing group depleting the electron density on the potential bridging hydrogens. In the case of thioboranes, the sulfur atom is expected to have the highest electron cloud. As a result, the intermolecular interaction with boron for polymer formation would be more favourable. Application of Sanderson's approach to phenylthioborane shows that the electron withdrawing effect of the aryl group reduces the electron density on sulfur in such a way that the interaction of sulfur with boron is not favourable.

In contrast, the reagent 1,3,2-dithiaborinane prepared from a reaction of borane-methyl sulfide complex with an equimolar amount of 1,3-propanedithiol,[67] was reported by O'Neill *et al.* [68] as an efficient reagent for direct conversion of carboxylic acids to 1,3 - dithianes in the presence of stannous chloride (Scheme 34).

[e] The Sanderson's calculations are discussed briefly in reference 61.



Scheme 34

Unfortunately very little information is available on these thioboranes as hydroborating agents. Of all these thioboranes, 1,3,2-dithiaborolane trimethyl amine complex has been reported as an effective hydroborating agent when treated with BF_3:OEt_2 in boiling benzene.[53]

1.4.3.5 Alkyldiaminoborane Chemistry

1,3,2-Diazaboracycloalkene (Figure 1.6) has been known for some time with previous work focusing mostly on the β-alkyl and -aryl derivatives of these heterocycles.[69]

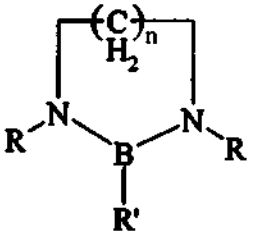
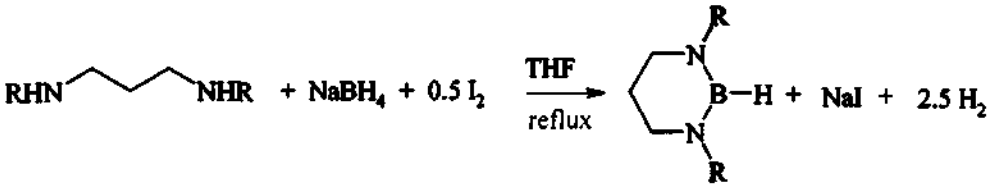


Figure 1.6

All β-halo derivates of this compound have been described.[70] 2-Hydrido-1,3,2-diazaboracyclohexanes can be synthesized by the method illustrated in Scheme 35.[71]



Scheme 35

The alternative route involves the use of trimethylamine borane complex as the source of the borane, with trimethylamine borane serving equally well as sodium borohydride.[71] In this method, trimethylamine is produced as a by-product and thus assists the purification of the desired heterocycles.

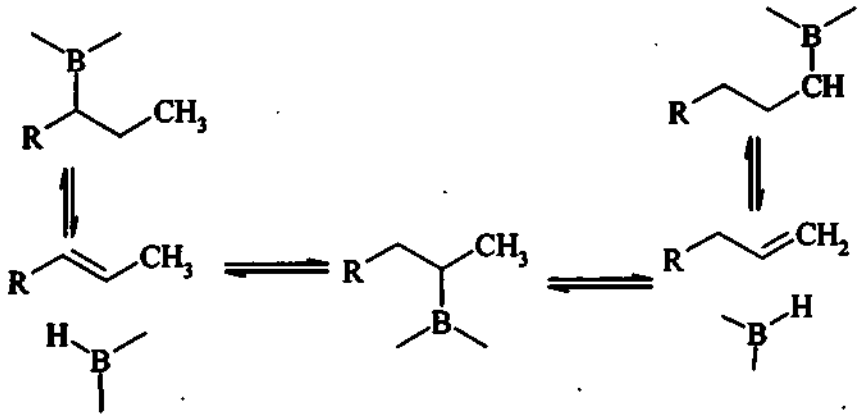
Before the above synthetic routes were discovered, only one parent compound with R' = H (Figure 1.6) was reported.[72] It was made from the trans-amination reaction of bis(dimethylamino)borane($H\text{-}B(N(CH_3)_2)_2$) with 1,3 diamino propane. In this case, no information has been reported on these systems as hydroborating agents.

1.5 Thermal Behaviour of Organoboranes

1.5.1 Isomerization

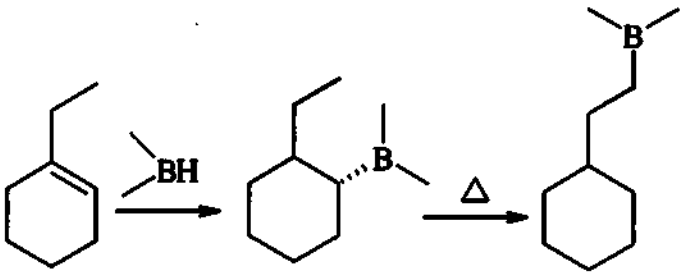
At 160 °C, the organoboranes undergo an isomerization involving the movement of the boron atom from an internal position predominantly to a terminal position or least hindered position of the alkyl group.[73]

The isomerization mechanism involves a partial dissociation of the organoborane into olefin and a boron-hydrogen moiety, this is followed by re-addition. This process takes place repeatedly until the boron atom ends up at the least hindered or terminal position of the molecule (Scheme 36).[9]



Scheme 36

This isomerization makes possible some simple but interesting synthesis. An example is the hydroboration product of β-pinene, tris(*cis*-myrtanyl)borane, which converts into the more stable *trans*-myrtanyl derivative upon treatment with heat.[74] It is also possible to move the boron atom from the ring to the side chain (Scheme 37).[74]

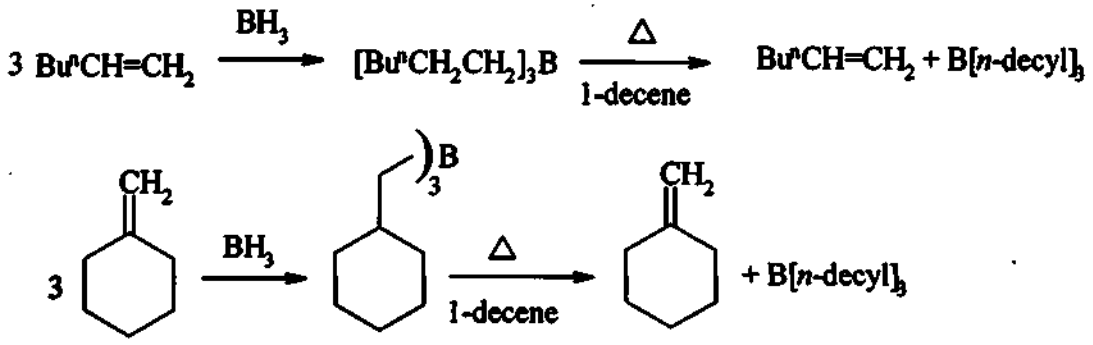


Scheme 37

Little attention (in the literature) has been based on the rates of isomerization, and one of the few examples is a comparative investigation of the rate of isomerization of β-alkyl-9-BBN derivatives and mono alkyldicyclohexylboranes, where the dicyclohexylborane derivatives have been shown to have greatly enhanced isomerization rates when compared to corresponding alkyl-9-BBN derivatives.[75] According to this observation it has been speculated that the isomerization rates may be highly influenced by steric factors.

1.5.2 Displacement

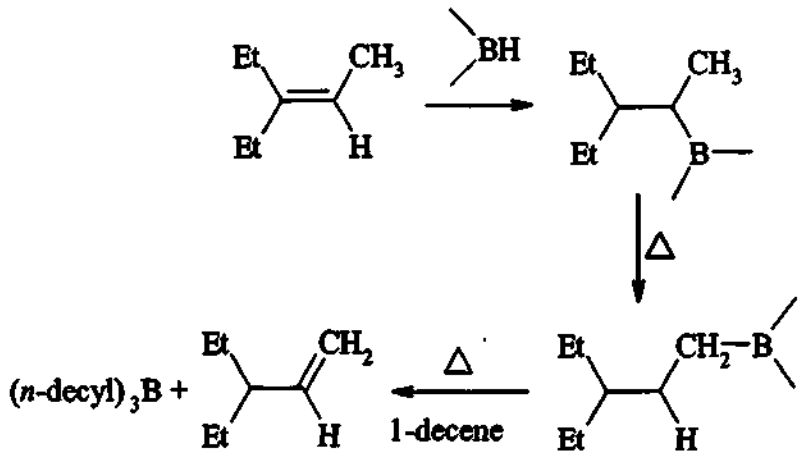
The proposed mechanism for the isomerization in Scheme 36 showed that isomerization involves a series of eliminations and re-additions of the boron-hydrogen moiety. Introduction of a second alkene into the reaction mixture results in the capture of the boron-hydrogen moiety. If a less volatile alkene is introduced, it becomes possible to distil out the original alkene as shown in Scheme 38 below.[76]



Scheme 38

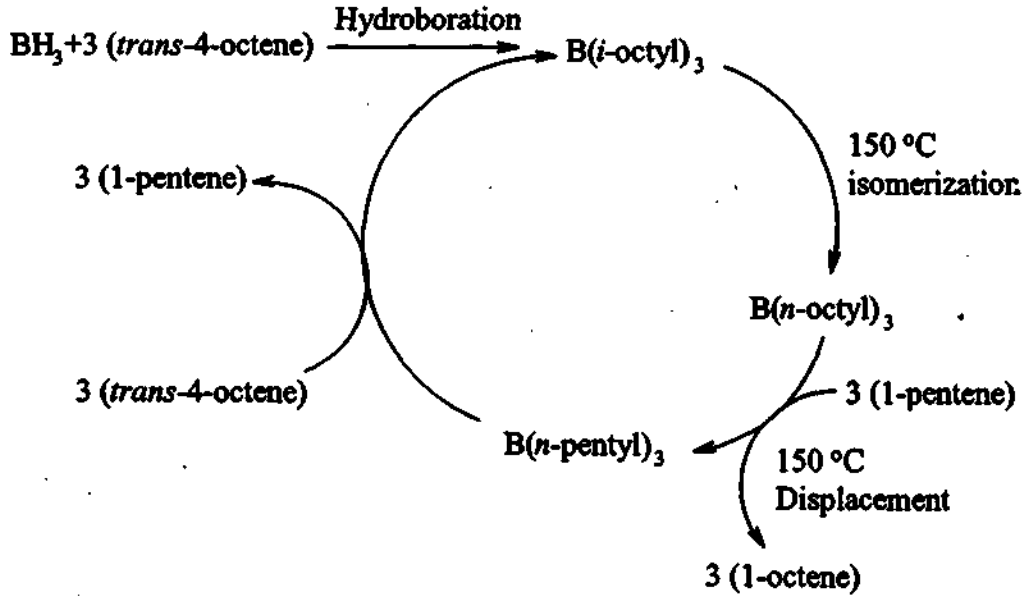
1.5.3 Contrathermodynamic Isomerization of Alkenes

A practical synthetic route for the contrathermodymic isomerization of olefins is achieved by a combination of hydroboration, isomerization and displacement.



Scheme 39

This combination has opened a possible synthetic route for producing a large number of 1-alkenes with various chain lengths from Sasol's readily available internal olefin feed stocks. The proposed contrathermodynamic cycle for the conversion of *trans*-4-octene to 1-octene is illustrated below (Scheme 40).



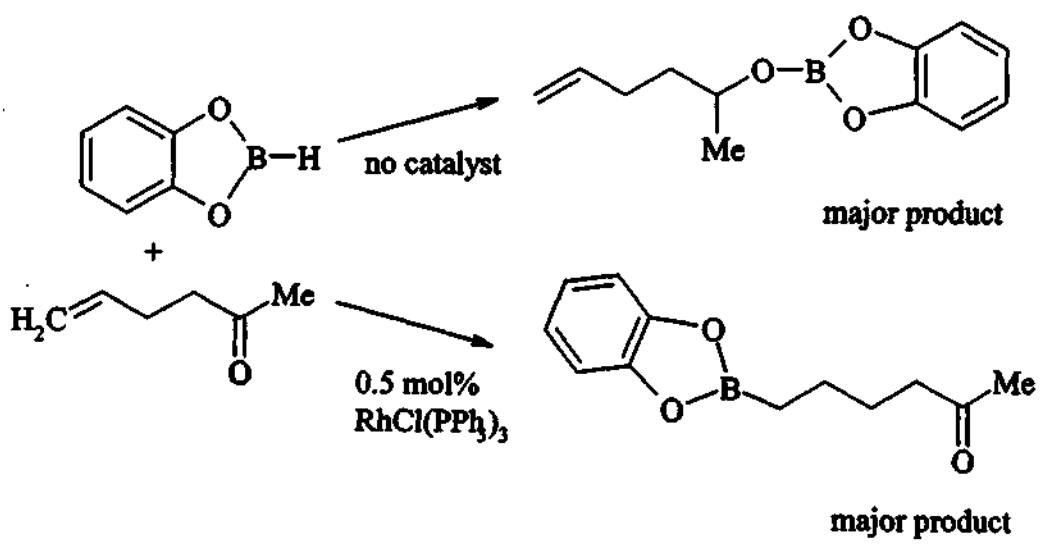
Scheme 40

1.6 Transition Metal Catalyzed Hydroboration of Olefins

1.6.1 Rhodium(I) Mediated Hydroboration with Catecholborane

As has been indicated previously in section 1.4.3.2, catecholborane hydroborates alkenes at a very slow rate at room temperature, this rate can be greatly elevated using a small amount of a transition metal complex.[77]

The chemoselectivity of reactions of multifunctional substrates can also be altered by catalysis. As an example, in a molecule with both olefinic and ketonic functional groups, catecholborane reacts with the ketone in the absence of the catalyst, while on the other hand hydroboration of alkene takes place preferentially in the presence of less than 1 mol % of $RhCl(PPh_3)_3$ (Scheme 41).[78]



Scheme 41

The catalyst $RhCl(PPh_3)_3$ provides alternatives for manipulating regio-, stereo-, and chemoselectivity in hydroboration processes.

For the hydroboration of terminal alkenes, the regioselectivity is the same for non-catalytic and catalytic reactions.[79] In both reactions the anti-Markovnikov product dominates. Figure 1.7 below shows approximate times for complete hydroboration at 20 °C of some alkenes with two equivalents of catecholborane and $RhCl(PPh_3)_3$ in THF.[80] The variation in rates is attributed to the steric hindrance.

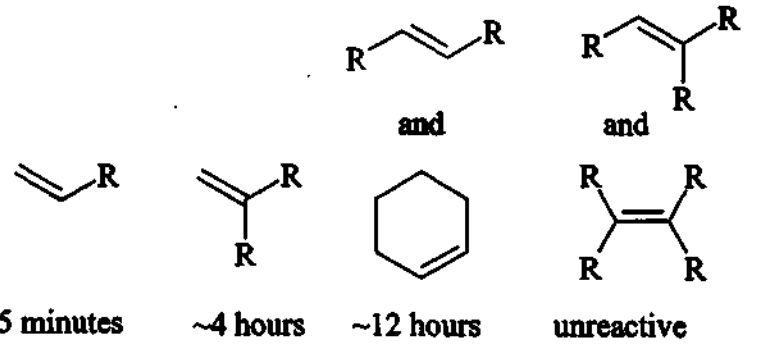
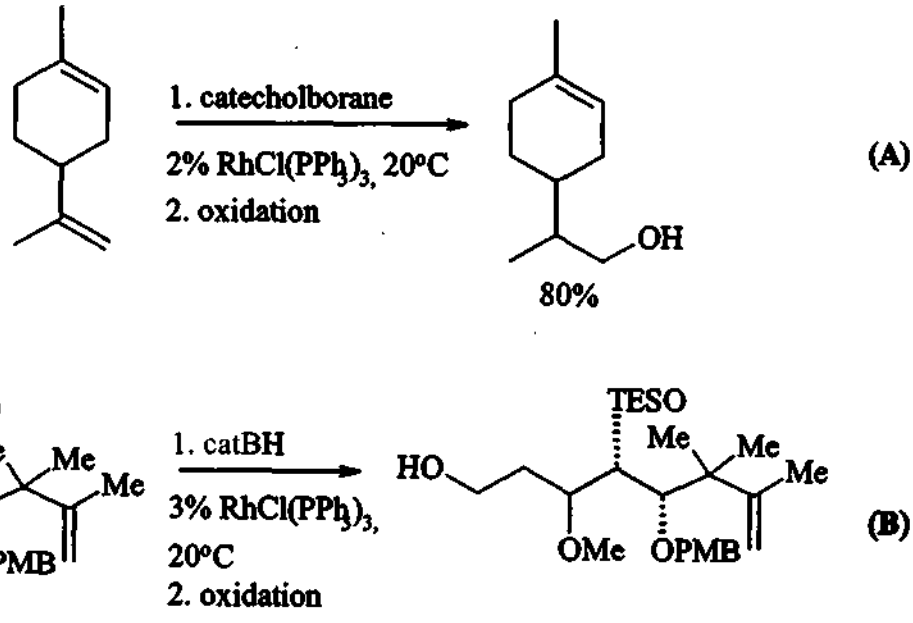


Figure 1.7

This large rate variation can be used in synthesis, for example in the hydroboration of limonene (Scheme 42 b)[81] and in the synthesis of calyculin A (Scheme 42 b).[81]

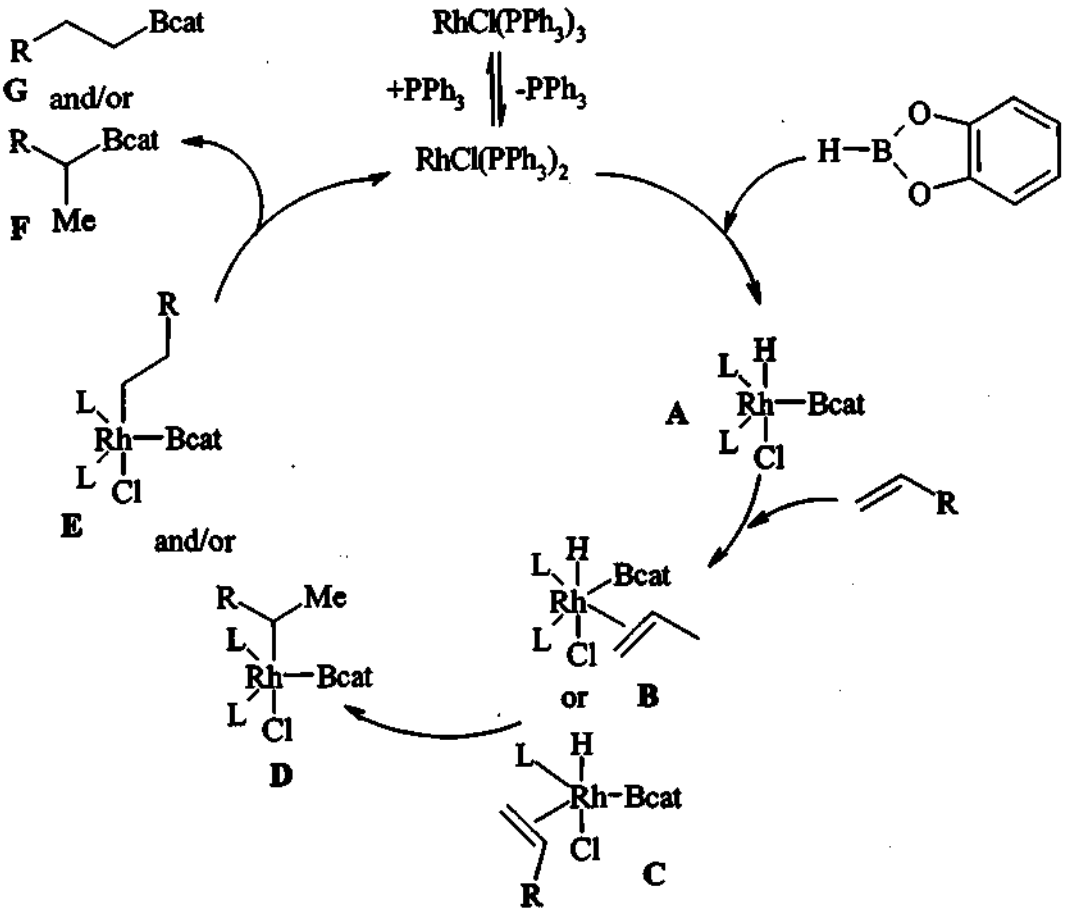


Scheme 42

1.6.1.1 Mechanistic Consideration of $RhCl(PPh_3)_3$ Catalyzed Reactions

The most efficient catalysts for hydroboration appear to be rhodium complexes of the Wilkinson type. A generalized mechanism for rhodium-promoted hydroboration is shown in Scheme 43.[78]

The first step is the insertion of the B-H bond to the coordinatively unsaturated metal center to give **A** which coordinates alkenes to give **B** or **C**. This is followed by the hydride migration which yields either **D** or **E** which in turn undergo reductive elimination to give respectively the anti-Markovnikov product **G** and/or the Markovnikov product **F** and the catalyst is regenerated to complete the cycle.



Scheme 43

A mechanistic investigation by Evans *et al.*[78] using deuteriocatecholborane revealed that there is a significant amount of deuterium at C_1 (from the reaction of 1-decene and deuteriocatecholborane in the presence of rhodium catalyst) showing that the migration of deuteride to the rhodium-bound alkene is only moderately regioselective. This study shows that it is in fact the reversibility of this step, coupled with high preference for reduction elimination of boron-primary alkyl rather than boron-secondary alkyl, which permits the nearly exclusive generation of the terminal alkylborane.

1.6.2 Rh(II) Catalyzed Hydroboration with Catecholborane

Rhodium(II) carboxylates and carboxamides are also effective catalysts for the hydroboration of alkenes with catecholborane.[82] In these systems THF is not used due to the fact that it coordinates with dirhodium(II) compounds, thus inhibiting the hydroboration reaction. These reactions are carried out in refluxing dichloromethane with 0.5 mol% of catalyst $Rh_2(OAc)_4$.[82]

Rhodium(II) diacetate can isomerize alkenes. Complete isomerization of allylbenzene to a mixture of (E) and (Z)-1-phenylpropene (81:19) was achieved in the presence of 1.0 mol% $Rh_2(OAc)_4$ and catecholborane (3.0 mol%). Neither $Rh_2(OAc)_4$ nor catecholborane alone caused isomerization, indicating the involvement of a rhodium hydride species.

1.6.3 Rh(III) Catalyzed Hydroboration with $NaBH_4$

Rhodium(III) octaethylporphyrin (OEP) is used in combination with $NaBH_4$ and molecular oxygen in the reduction of carbonyl compounds.[83] The same combination has been applied to the hydroboration of alkenes and alkynes.[83] This unique system gave interesting results; alcohols are produced directly from either alkenes or alkynes. The system is cheap, has no need for inert atmosphere and dry solvents, thus making this system easy to use.

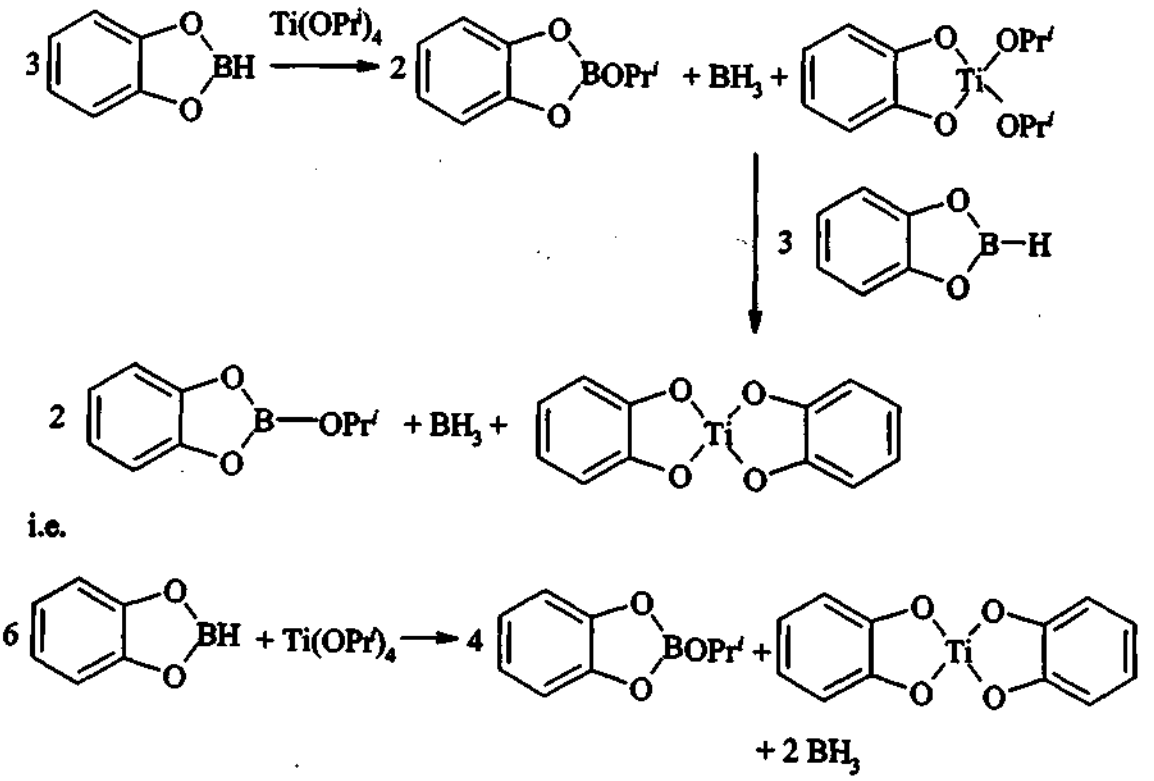
1-Octanol and 2-octanol are produced from 1-octene in the ratio 91:9. Little regioselectivity is observed in the hydroboration of styrene. The primary to secondary alcohols ratio is 61:39; 1-heptene yields 1- and 2-heptanol in the ratio 82:18.

The mechanism of this reaction is by no means clear.[84] It is suggested that (OEP)Rh(III)BH_4 could act as a source of borane and (OEP)RhH. The latter could then react with oxygen yielding (OEP)RhOOH and this could behave like ^-OOH and oxidize alkyboranes formed during hydroboration.

1.6.4 Titanium-Catalyzed Hydroboration with Catecholborane

A number of research groups have investigated catalytic hydroboration with early transition metal complexes in order to seek new catalytic pathways and to reduce the cost of hydroboration.[85,86] Many studies have suggested that the rate of addition of catecholborane to olefins can be enhanced by early transition metal systems.[77 - 86]

Cp_2TiCl_2[87] and $TiCl_3$[88] are also known to promote hydroboration of alkenes by borohydrides. This case has recently been reinvestigated and it was found that $TiCl_3$ causes rapid dismutation of $LiBH_4$ to borane which is the active hydroborating agent.[89] Borane is produced *via* $Li[Cp_2Ti(BH_4)_2]$ if Cp_2TiCl_2 is used.[89] In some cases Cp_2TiH can add across a double bond.[89] Hydroboration of alkenes by catecholborane was also catalyzed by titanium tetraisopropoxide ($Ti(O\text{-}Pr^i)_4$). This was also due to the formation of borane (Scheme 44).[89]

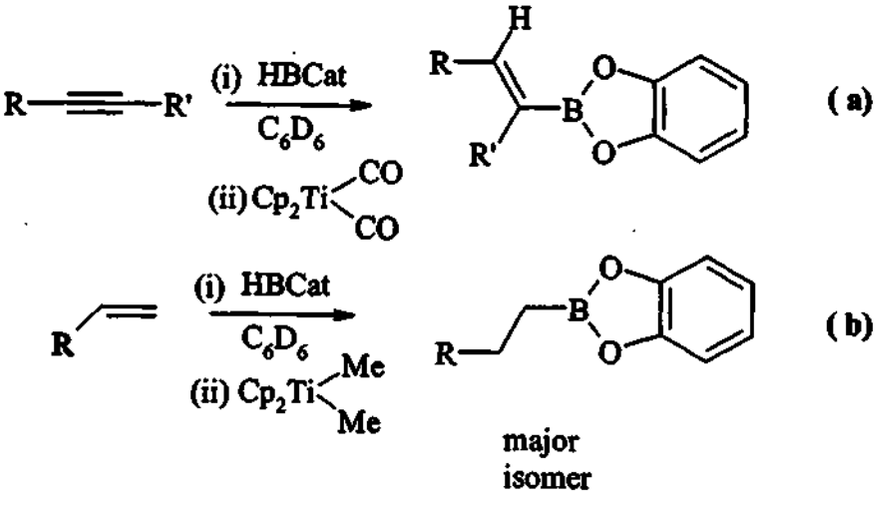


Scheme 44

Burgess and Van der Donk also found that $(Mesitylene)_2Nb$ catalyzes decomposition of catecholborane to diborane and B_2Cat_3 (Cat= $O_2C_6H_4$).[90] The produced diborane in turn provides the hydroboration. Therefore, these early transition metal complexes are not "true" hydroboration catalysts.[91]

1.6.4.1 Hydroboration of alkynes with $Cp_2Ti(CO)_2$

The reaction of the alkyne with 1.0 equivalent of catecholborane in the presence of 4 mol% of dicarbonyltitanocene resulted in a complete conversion of alkyne after 2 hours at 25 °C into vinylboronate ester (Scheme 45 a).[85] Anti-Markovnikov products were formed exclusively with terminal acetylenes. The observed regioselectivity is higher than that for the uncatalyzed reaction at elevated temperatures (91:9 for phenylacetylene and 93:7 for 1-pentylene),[92] it is even greater than that observed for the Wilkinson's catalyst.[85] Xiaoming and Hartwig[85] observed that no trivinylborane products were formed from uncatalyzed diborane reaction chemistry and this led to the conclusion that the addition of catecholborane to alkynes catalyzed by dicarbonyltitanocene is a true metal-catalyzed hydroboration as opposed to reactions catalysed by other titanium containing catalysts discussed in the preceding section.



Scheme 45

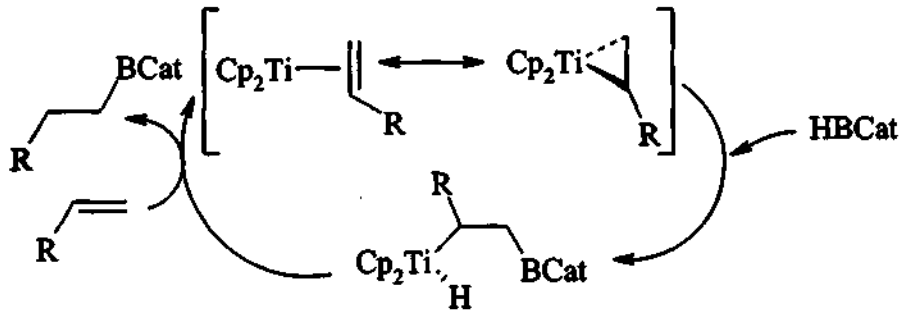
1.6.4.2 Hydroboration of alkenes with Cp_2TiMe_2

Hydroboration of alkenes catalyzed by dimethyltitanocene requires a ligand substitution process whereby one carbonyl ligand is displaced by an alkene and this substitution reaction is less favourable than displacement by an alkyne.[85] Xiaoming and Hartwig showed that the addition of catecholborane to alkenes catalyzed by $Cp_2Ti(CO)_2$ was slower than addition to alkynes unless CO dissociation was induced photochemically (using a standard medium pressure Hanovia arc lamp). This led to the use of bis(cyclopentadienyl)titanium dimethyl, also known as dimethyltitanocene (Cp_2TiMe_2) as an alternative source of titanocene fragment (Scheme 45 b).[85]

Further studies by Xiaoming and Hartwig[85] showed that terminal alkenes were hydroborated at room temperature. Internal alkenes were hydroborated at 55 °C in essentially quantitative yields. Anti-Markovnikov products predominated and were formed entirely for aryl-substituted alkenes. In the early 1990's Westcott *et al.*[93] reported that hydroboration of styrene catalyzed by rhodium yields the Markovnikov product and this contrasts the observations of Xiaoming and Hartwig of the anti-Markovnikov selectivity in the hydroboration of styrene catalyzed by dimethyltitanocene (Cp_2TiMe_2).

1.6.4.3 Mechanistic Consideration of Titanium Catalysed Reactions

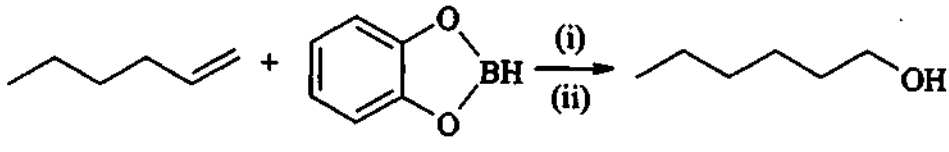
A proposed mechanism for the catalyzed addition of catecholborane to alkenes is shown in Scheme 46 below.[85] The proposed mechanism is likely to proceed by σ-bond metathesis between catecholborane and one Ti-C bond of a titanium alkene or alkyne complex that adopts a significant metallacyclopropane or propene character due to the strong back bonding ability of d^2 metals.[94]



Scheme 46

1.7 Organolanthanide Catalyzed Hydroboration of Olefins

In early 1990's Harrison and Marks[95] reported that organolanthanides are effective homogeneous catalysts for olefin hydroboration (Scheme 47) and disclosed initial observations on scope, selectivity, and mechanism.

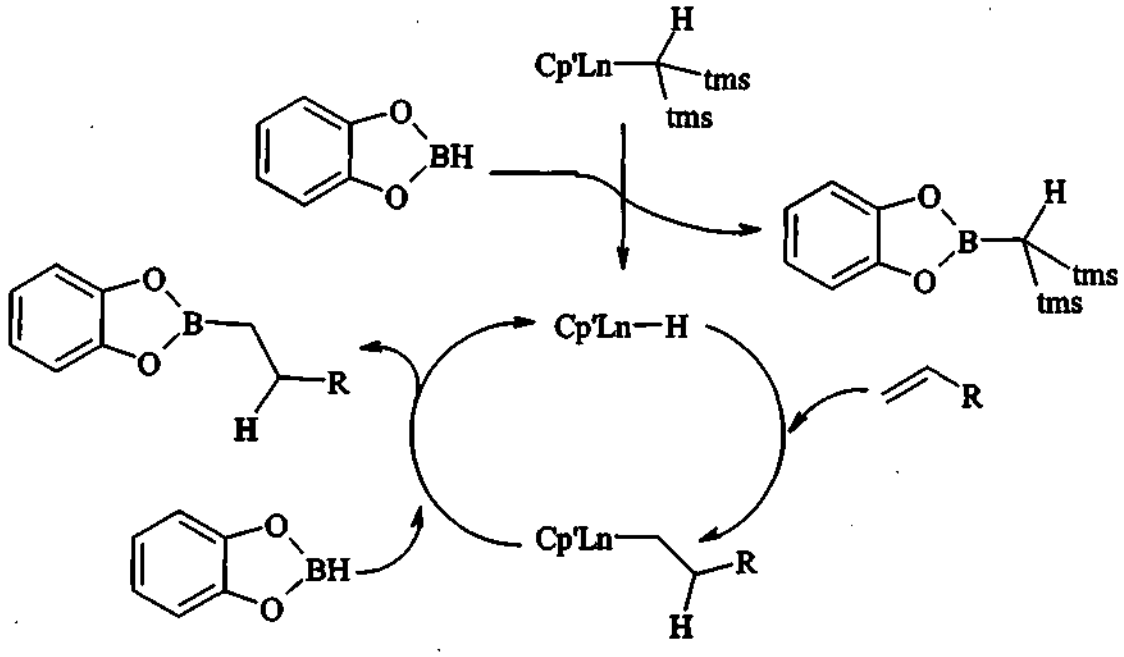


(i) Cp'LnR, 25 °C
(ii) H_2O_2, NaOH

Scheme 47

Where Cp'= η^5-Me_5C_5; Ln = La, Sm; R = H, $CH(SiMe_3)_2$, these complexes catalyze hydroboration of a variety of dry degassed olefins (25-100 fold stoichiometric excess) with catecholborane at efficient rates at room temperature.[95] The reaction includes a range of olefinic substrates, these involve terminal, internal disubstituted and trisubstituted species. High regioselectivity (> 98% by NMR spectroscopy) is observed for all these organolanthanide-catalyzed transformations.[95] The observed regiochemistries are exclusively anti-Markovnikov. Harrison and Marks[95] observed the anti-Markovnikov products in the organolanthanide catalyzed hydroboration of styrene which contrasts the

general pattern observed for rhodium catalyzed hydroboration of styrenes.[93, 96] Shown in Scheme 48 is the proposed mechanism for organolanthanide-catalyzed hydroboration.[95]



Scheme 48

1.8 Project Aims

The project was designed to explore the reactivity of a range of electron deficient heteroatom containing borolanes towards selected alkenes. Parts of these studies were directed towards the synthesis and ^{11}B NMR spectroscopic analysis, of a range of sulfur, nitrogen and oxygen analogues (figure 1.8), which in turn were to be evaluated in terms of their reactivity towards selected alkenes. The study was also expected to shed light on the suitability of these reagents to mediate isomerisation and final displacement of the borolane to form the alkene. These results would ultimately assist in the potential evaluation of such electron deficient borolanes as possible reagents in a final industrial process for the commercial production of terminal alkenes.

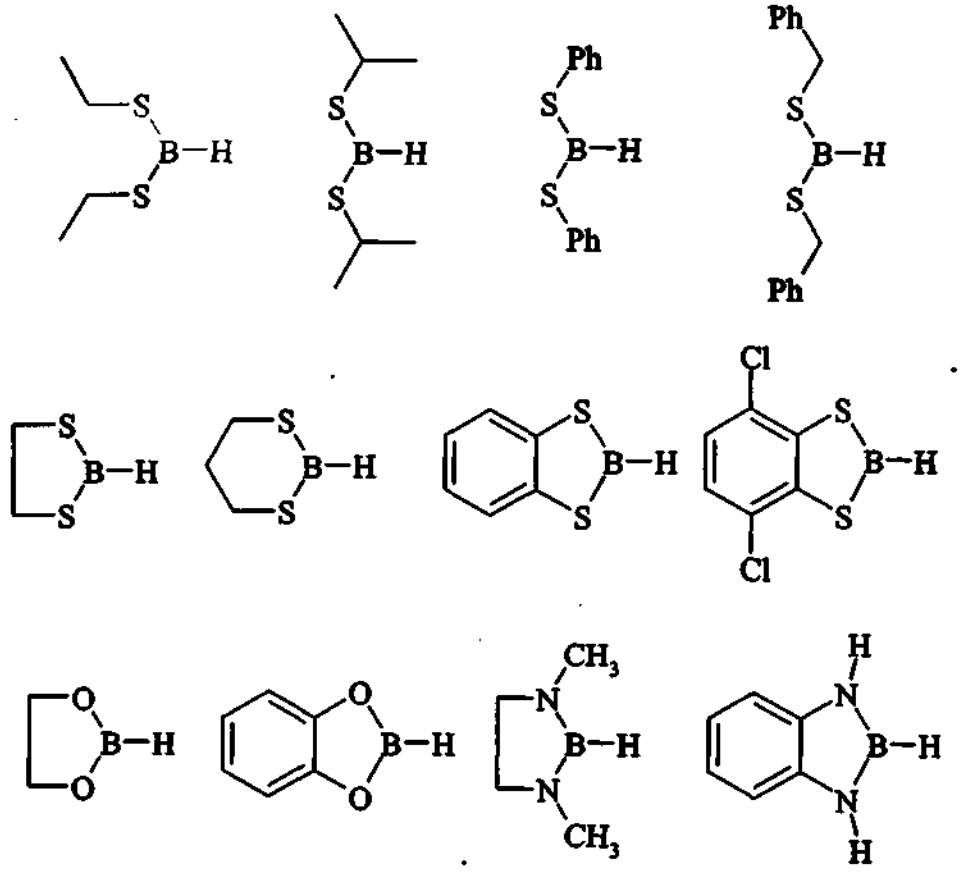


Figure 1.8

Chapter 2.

Instrumentation

2. INTRUMENTATION

In this section a brief introduction to the instrumentation used in this study will be reviewed, with the aim of illustrating both the limitations and applications of these techniques.

2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

2.1.1 Introduction

NMR spectroscopy is a very powerful tool that has found wide application in chemistry, most notably organic and biological chemistry. NMR spectroscopy involves the study of the nuclei of certain atoms when placed in a strong magnetic field and subsequently exposed to an oscillating magnetic field (the magnetic component of externally applied radiofrequency irradiation). The spectrum subsequently obtained from an NMR spectrometer is able to provide information about the structural and conformational backbone of the compound being studied hence its importance in chemistry.

Mostly frequently, use is made of one dimensional (1D) NMR spectroscopic techniques, to study chemical structures, while more complicated molecules are studied in conjunction with 2D techniques such as correlation spectroscopy for example. Many new applications for this technique are being explored on a daily basis and recently structural and conformational elucidation of proteins have been explored. This has been a revolutionary breakthrough as techniques such as x-ray crystallography which have been used in the past to study proteins rely on suitable crystals being grown in order to analyse them.[97] Another important technique explored is time domain NMR spectroscopy - this technique is used to investigate molecular dynamics in solutions, in this type of technique only time domain data can be acquired and relaxation time constants are correlated to physical properties of the mixture. On the other hand the molecular structures in solids

are determined using solid state NMR spectroscopy though this has found limited application to date.

2.1.2 Theoretical basis of NMR spectroscopy

The first successful proton NMR experiment was conducted in 1946 by Bloch and co-workers, and thus NMR spectroscopy was born.[98] Since these early days the technique has been developed to a great extent and one is able to study a wide variety of nuclei with different spin states.[98]

It has been shown that some atomic nuclei such as the hydrogen nucleus ^{1}H or phosphorus nucleus ^{31}P possess a property called spin, which is designated by the spin quantum number I. This property can be thought of as a spinning motion of the nucleus about its own axis (Figure 2.1).[99] Associated with this spin is an induced magnetic moment or dipole moment, that one could visualise as a tiny bar magnet with its axis lying along the axis of rotation of the nucleus.

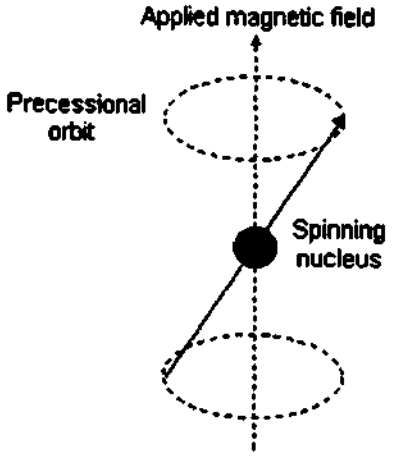


Figure 2.1: Showing a nucleus visualized as spinning about its own axis which is the axis of its magnetic moment

Those nuclei such as ^1H have a spin spin quantum number I = ½ and can thus have two orientations or spin states with respect to the applied magnetic field designated as -½ and +½. Under normal circumstances, in the absence of an externally applied magnetic field, the individual nuclei are randomly oriented. However, in the presence of a strong applied magnetic field the, nuclei with spin +1/2 align themselves along the field. On the other hand the nuclei with spin -1/2 orient themselves in such a way that their magnetic fields are against the applied field that is, in opposite direction to the applied magnetic field (Figure 2.2).[98]

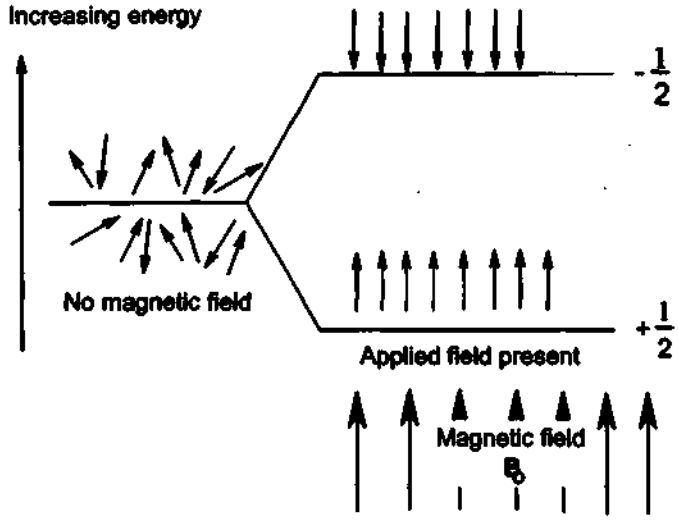


Figure 2.2: On the left, the spins of nuclei are randomly oriented in the absence of an applied magnetic field and on the right the presence of an applied magnetic field, the spins line up with or against the field.[100]

Those nuclei that are aligned with the magnetic field are said to be in the α- spin state while those nuclei that align against the field are in β-spin state. The nuclei in α-spin state are in lower energy than those in β-spin state. The number of nuclei in both spin states is almost the same since for every million there are about 10 to 20 more in the α-spin state (lower in energy) at room temperature. If electromagnetic radiation of the appropriate frequency is applied to the sample the nuclei are able to absorb this energy and flip from

the α-spin state into β-spin state. Before entering the discussion of the flipping of the α-spin state nuclei, it is important to first look at a brief explanation of electromagnetic radiation.

James Clerk Maxwell[101] was the first to develop the electromagnetic theory, over a century ago, which provided explanation of a wide range of phenomena including magnetic and electric fields.[101] The more interesting feature about this theory is that it provided an explanation of the wave propagation of light. It also predicted the electromagnetic disturbance travels at the speed of light.[101]. Electromagnetic radiation is simply the disturbance consisting of coupled oscillating electric and magnetic fields that are perpendicular to each other and to the direction of propagation of radiation (see Figure 2.3 which represents this on a Cartesian plane).

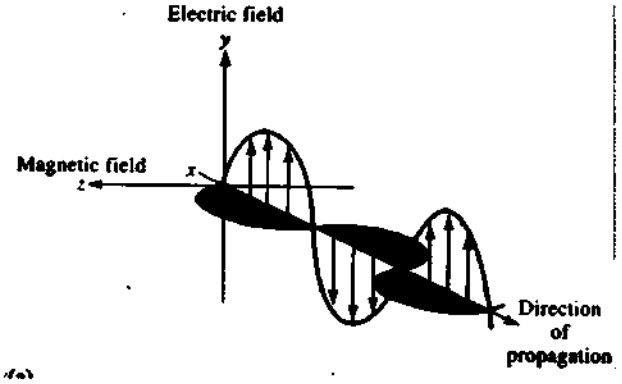


Figure 2.3: This Figure illustrates a beam of monochromatic, plane-polarized radiation with the electric field and magnetic field perpendicular to each other and the direction of propagation.

It is interesting to see that if the electromagnetic radiation of appropriate energy is applied to nuclei that were previously aligned by the applied magnetic field, the α-spin state nuclei absorb the radiation and flip its spin and simultaneously entering the β-spin state. The NMR spectrum is observed due to the detection of the absorption of the

electromagnetic radiation by the nuclei in the α-spin state (i.e. low in energy). The energy of the absorbed radiation equals the energy difference between the two states; this energy is released as heat when the molecule returns to the α-spin state. Due to the fact that nuclei are flipping back and forth between the α-spin state and the β-spin state because of the electromagnetic radiation, these nuclei are said to be in resonance with the electromagnetic radiation so this is where the term nuclear magnetic resonance came from. The difference in energy (ΔE) between these two spin states is given by Equation 1.2,

$$\Delta E = h\nu = h\frac{\gamma}{2\pi}B_o$$

Equation 1.2

In the above Equation γ is the gyromagnetic ratio (in $radT^{-1}\ s^{-1}$) also known as the magnetogyric ratio.[101] Its formal definition is that it is the ratio given by the magnetic moment of the spinning particle to its angular momentum. Its magnitude varies from one nuclei isotope to another, in other words, it depends on the particular kind of a nucleus. h is Plank's constant, ν is the frequency, and B_o is the externally applied magnetic field.

From this Equation (Equation 1.2) it is evident that the energy difference between the two spin states depends on the strength of the externally applied magnetic field (B_o) (Figure 2.4). Figure 2.4 illustrates the fact that greater the difference of the applied magnetic field the greater the energy difference.[98]

Since the gyromagnetic ratio varies from one kind of the nucleus to another so the NMR spectrometer requires different energy sources in order to bring different kinds of nuclei into resonance with a given operating frequency.

The ^1H proton nuclei absorbs energy when the gap (ΔE) between the two spin states equals the operating frequency of the spectrometer. A potential problem could arise if all the protons within a particular organic compound were in the same magnetic

environment. As a result they would all resonate at the same frequency, and the NMR spectrum would consist of a single line. Typically, this scenario is not encountered since protons are often located in different environments with varying electron density around them which either shields or de-shields them from the externally applied magnetic field. This results in different groups within a particular compound resonating at different frequencies within the NMR spectrum.

The same effective magnetic field is required for all protons in a compound, this effective magnetic field can be defined as the magnetic field that is sensed by the proton.[98] It is important to note that a much stronger applied magnetic field is required for more shielded protons so that they can sense the given effective magnetic field, whereas for less shielded protons a weaker applied magnetic field is required for them to feel the same effective magnetic field (Figure 2.5).[98]

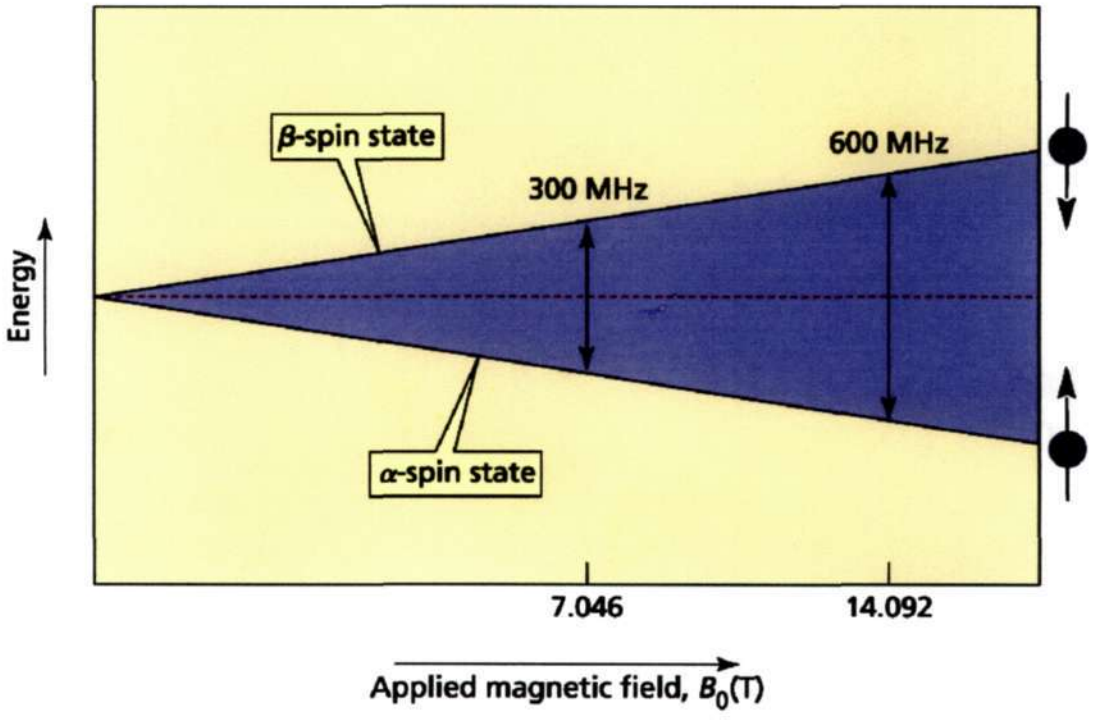


Figure 2.4: The greater the strength of the applied magnetic field, the greater the difference in energy (ΔE)

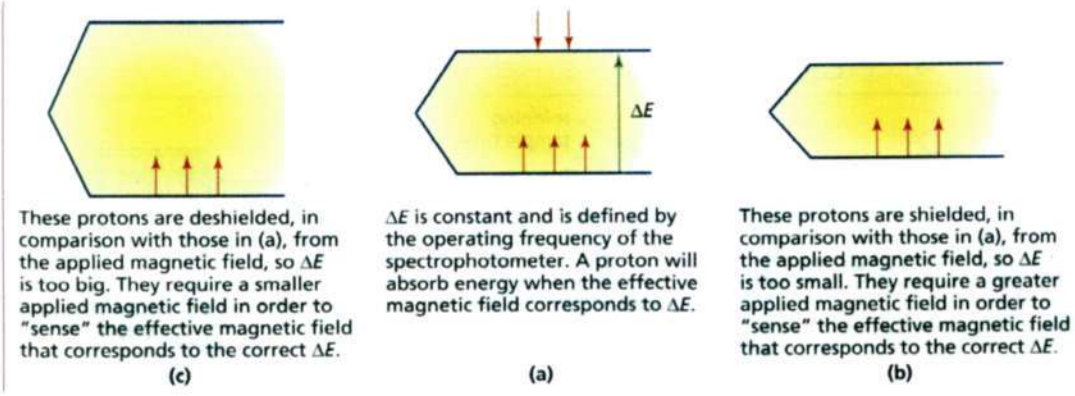


Figure 2.5: Showing the protons in a shielded and a deshielded environment.[98]

A mathematical description is shown in Equation 2.2, where $\boldsymbol{B}_{\text{eff}}$ is the total effective field at the nucleus and $\boldsymbol{B}_o$ is the applied field and σ is a dimensionless constant, known as the shielding constant, its magnitude depends upon the electronic environment of the nucleus. As a result, nuclei in different chemical environments give rise to signals at different chemical shifts (δ).[101] The chemical shift is defined as the difference between the resonance frequencies of the nucleus from that of an arbitrarily chosen reference nucleus most often tetramethyl silane (TMS), and is expressed in parts per million (ppm).

$$B_{eff} = B_o(1-\sigma)$$

Equation 2.2

A technically easier method used in NMR spectroscopy in early days was to keep the frequency constant and slowly vary the applied magnetic field, as a result this brings a change in the energy separation between the α-spin state and the β-spin state. The applied magnetic field is adjusted until the energy separation between the two spin states match the operating frequency of the spectrometer.[98] A simple analogy to the above description is tuning the radio frequency until the right station is found. In NMR spectrometers protons absorb energy from radio frequency source, radio waves are indicated in the

electromagnetic spectrum shown in Figure 2.6, they are found at a wavelength of about $10^6 \sim 10^{10}$ μm.

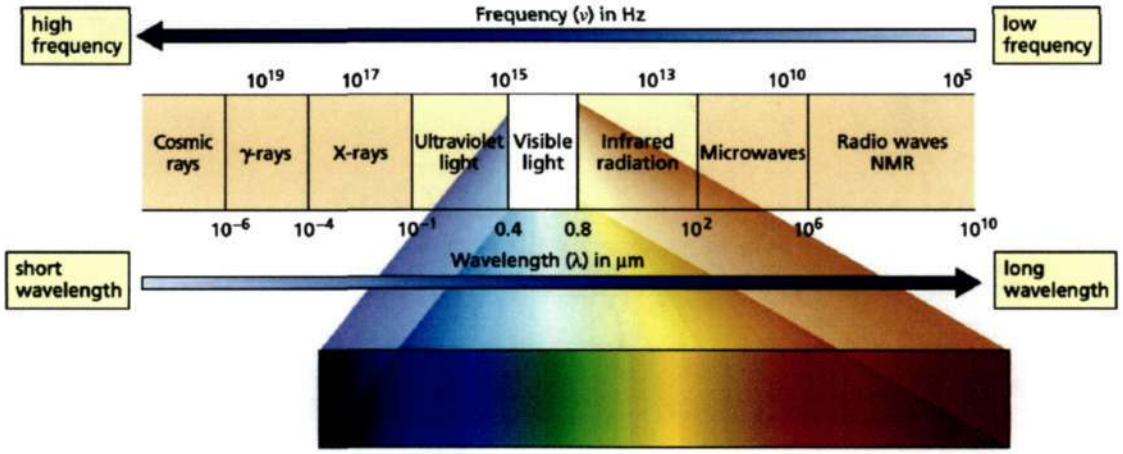


Figure 2.6: showing the electromagnetic spectrum.[98]

Two instruments, which operate with two different techniques, are commonly used in obtaining the NMR spectrum, these are the continuous-wave (CW) spectrometer and the more modern pulsed Fourier transform (FT) spectrometer.

In a CW spectrometer a magnetic controller is used to vary the strength of magnetic field continuously. When the nuclei in the molecule flip their spin, signals are detected and recorded as a spectrum. However, this technique is passive when compared to a FT-NMR spectrometer, in this technique all nuclei are excited at the same time by a very short radio-frequency (rf) pulse of short period of time. All the signals are collected simultaneously and compiled by a computer, and here many hundreds of individual scans

are obtained in less than a second and averaged. The information is converted mathematically into a spectrum. The FT-NMR spectra differ from those obtained from the CW spectrometer due to the fact that the FT-NMR spectrometer has excellent signal-to-noise ratios that result in clear well resolved signals. FT-NMR is also more sensitive and much faster than the CW NMR, these are two important advantages of the FT-NMR.

In FT-NMR, the radio frequency field is applied in short powerful pulses with a bandwidth large enough to excite all nuclei in that particular spectral window. After the response is observed, the process is repeated a number of times at intervals of typically 1 second. The pulse intervals depend upon the values of the spin-lattice relaxation times[101]. The spin-lattice relaxation (designated by T_1) is described as the process of transferring spin energy to the surrounding lattice.[100]

The observed responses are automatically accumulated in a computer until the required signal-to-noise ratio is established; the computer program then conducts a Fourier transformation of the data to produce the final spectrum. These responses decay exponentially as all nuclei undergo relaxation. This process is named the free induction decay (FID).[101]

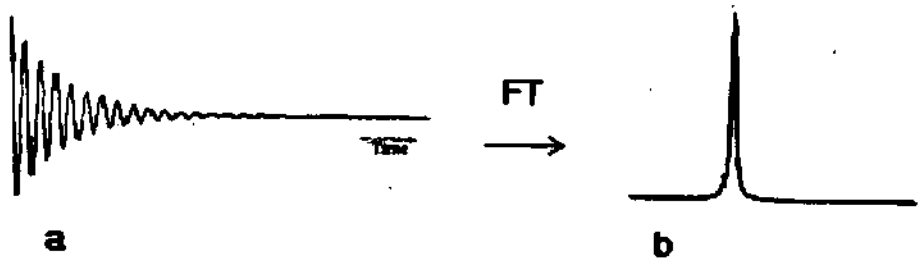


Figure 2.7: (a) shows a time domain FID obtained after an rf pulse, (b) shows a frequency domain NMR signal obtained after a Fourier transformation manipulation.

The NMR spectrum is obtained by dissolving about 5 to 50 mg of a sample in approximately 0.5 ml of an appropriate solvent.[98] Deuterated solvents such as $CDCl_3$ and D_2O are typically used since their signals are not seen in ^1H NMR spectrum. The solution is then transferred into a long and thin glass NMR tube which is placed in the magnetic field. In order to get a higher resolution of the spectrum, the sample tube is allowed to spin along its axis. This will average the molecules with respect to their positions in the magnetic field between the poles of the magnet. The sample in a spinning tube is irradiated with radio frequency from the transmitter as shown in Figure 2.8.

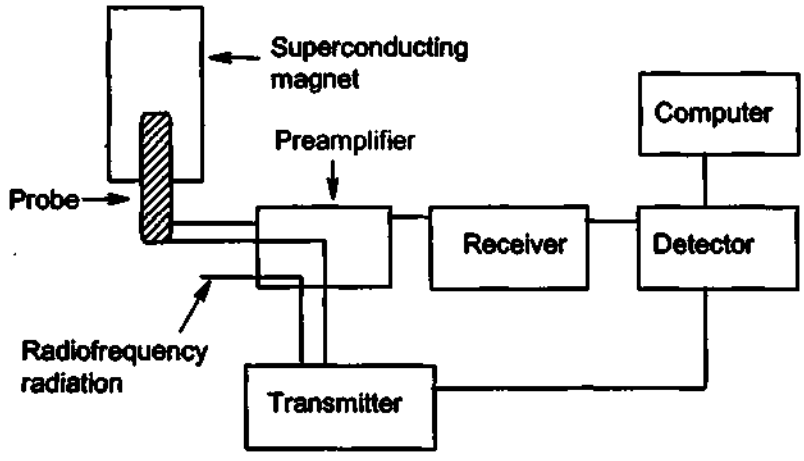


Figure 2.8: Schematic representation of an NMR spectrometer.[102]

To date, superconducting magnets (Figure 2.9) are used in NMR instruments to produce higher field strengths of about 470 MHz (Figure 2.9) to 750 MHz,[103] and very recently up to 900 MHz (Figure 2.10). Advantages of using more powerful magnets are: -

I. The increase in field strength improves the signal-to-noise ratio and this leads to better resolution.
II. Provides more information on the structure of molecules, allowing the detection and characterization of more complex compounds and significantly lower quantities of sample needed.

In its simplest form, this means that more powerful magnets simplify the appearance of the spectra which in turn allows for more accurate interpretation of the spectra.

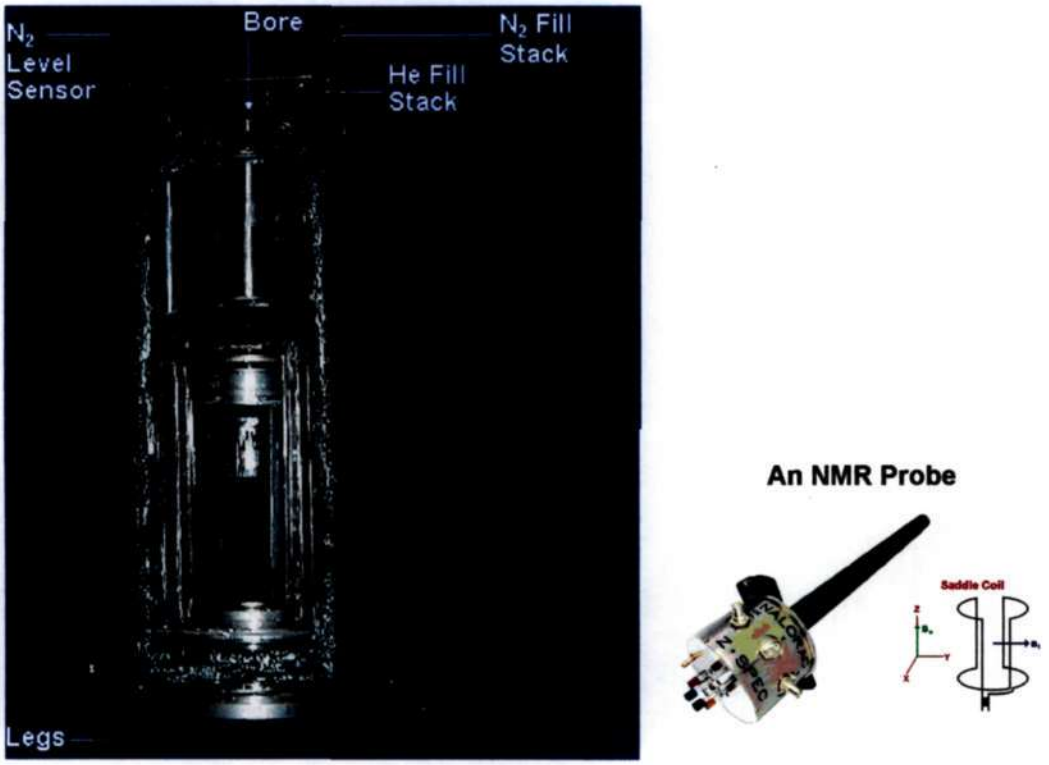


Figure 2.9: On the left, shown is a high field superconducting magnet (470 MHz) and on the right is an NMR probe located within the magnetic solenoid assembly that is totally immersed in liquid helium at -269 ^{o}C. Vacuum tank and liquid nitrogen provide insulation to minimize liquid helium evaporation.[100]

Figure 2.10: A 900 MHz NMR superconducting magnet, manufactured by Varian NMR systems and Oxford Instruments.

2.1.3 ^{11}B NMR Spectroscopy

^{11}B NMR spectroscopy has been used by chemists for some time for structural elucidation and has become as routine and versatile as ^{19}F and ^{31}P NMR spectroscopy.[104] ^{10}B and ^{11}B are the two naturally occurring boron isotopes and they are both suitable for boron NMR studies as they possess a spin quantum number $I \neq 0$ and are thus NMR active (refer to Table 2.1). In addition to this, ^{11}B has a high degree of abundance *ca.* 80% (Table 2.1) and a greater gyromagnetic ratio than ^{10}B and thus has a better sensitivity to NMR experiments. These features make it preferable to observe the ^{11}B nuclei in the spectrometer.[104]

Table 2.1: Nuclear properties of some isotopes.

Nucleide	Natural abundance %	*I*	Gyromagnetic Ratio γ (x10^7 radians $s^{-1}T^{-1}$)	Resonance frequencies at 2.3010 *T* (MHz)
^{1}H	99.98	½	26.76	100.00
^{10}B	18.83	3	2.875	10.53
^{11}B	81.17	3/2	8.582	32.08
^{13}C	1.11	½	6.725	32.14
^{14}N	99.64	1	1.933	7.22
^{15}N	0.36	½	-2.711	10.13
^{19}F	100	½	25.17	94.08
^{17}O	0.037	5/2	-3.628	12.71
^{35}Cl	75.53	3/2	2.621	9.60

^{10}B spectra are also easily obtained and these have been extensively used in labelling studies in order to elucidate and study reaction mechanisms.[104] Since the boron isotopes have a nuclear spin ≥ 1, quadrupolar broadening of the resonance signals is typically observed. The line width may be used to determine the relaxation times and the structure of the compound under investigation.[104] In a uniform magnetic field, B_o, an arbitrarily chosen nucleus can have $2I + 1$ possible orientations relative to the applied field.[105] Each orientation has its own energy level as expressed in Equation 3.2.[105]

$$E = -\gamma\hbar B_o \frac{M}{2\pi}$$

Equation 3.2

γB_o Is the angular velocity of a nucleus precessing about the applied magnetic field, M has values: $I, I-1, I-2, \ldots .- I$. The ^{11}B nucleus has a spin of 3/2, thus if we consider the interaction of a single ^{11}B nucleus with a single ^{1}H nucleus in a magnetic field, the ^{1}H nucleus "sees" four different fields, M = 3/2, 1/2 , -1/2, -3/2,[106] as a result the ^{1}H NMR

spectrum of B-H coupling will be a quartet with all four peaks of equal intensity.[105] The ^{1}H nucleus has a spin of 1/2 thus, from the standpoint of ^{11}B nucleus; ^{11}B nucleus will see two different fields. This results in an ^{11}B nucleus being in either of the two fields. The first one is where the ^{1}H spin parallel to the external field, and the second one is where the ^{1}H spin antiparallel to the external field. Thus, the ^{11}B NMR absorption will be a symmetrical doublet.

Most ^{11}B NMR spectra involve coupling of the boron nucleus with a proton. Boron-boron coupling is not observed due to the large quadrupolar moment which leads to broadening of the resonance signal in the ^{11}B NMR spectrum. The number of signals is determined by the $2nI + 1$ rule, for coupling with protons. In this rule, n is the number of protons bonded to the boron atom, and I is the ^{1}H spin quantum number. For example, the coupling of ^{11}B and ^{1}H nuclei in BH_4^-, result in a symmetrical quintet ($2nI+1= 5$ lines) with relative intensity pattern of 1:4:6:4:1 (Refer to Figure 2.11).[105]

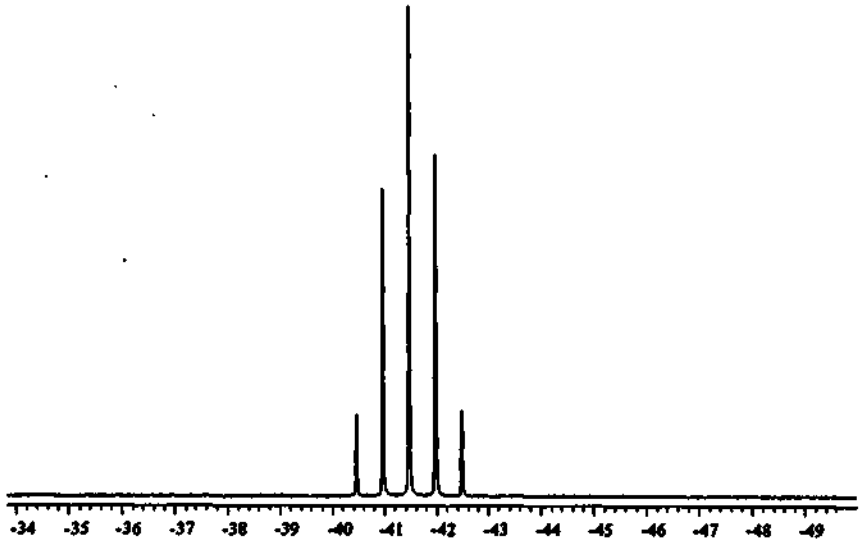


Figure 2.11 ^{11}B NMR spectrum of $NaBH_4$ in diglyme.

The chemical shifts observed in the ^{11}B NMR spectrum depend on a number of factors such as the nature of the substituents on the boron atom, charge, and coordination number.[104] This can give valuable information about the structure of the compound,

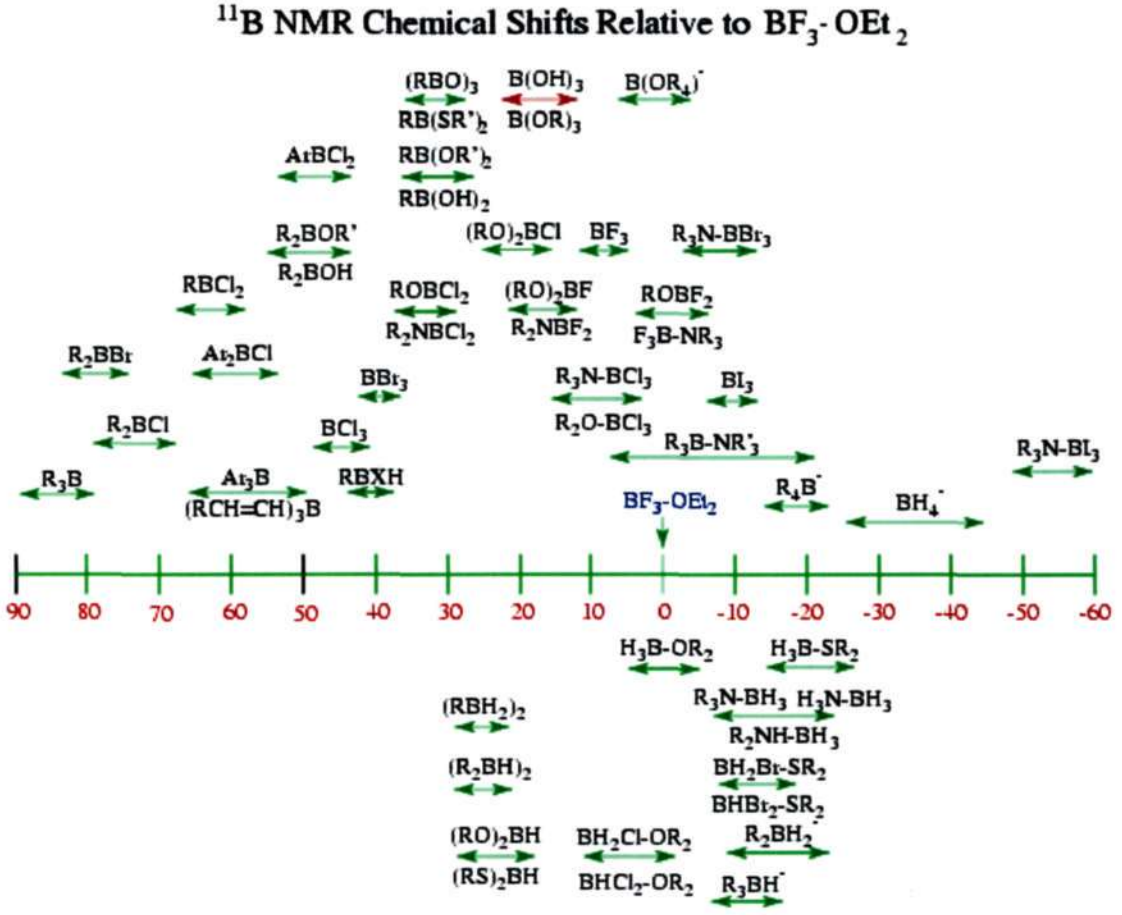
composition and about reaction mechanisms. The chemical shifts of the trialkylboranes are found in a low field region, 83 – 93 ppm, and these are independent of the structure of the alkyl group, while on the other hand cyclic boranes show a remarkable dependence on the sizes of the ring.[104] The borinanes, six membered boron-containing rings, all show similar chemical shifts as the acyclic compounds.[104] The ring size affect the chemical shifts for all cyclic boranes irrespective of the substituents present.[104]

^{11}B resonances are shifted to higher fields if :[107]

i. the α-carbon R_2BCH_2X is substituted with X= N_3, OH, NH_2, Cl, Br, I, PMe_3, $AsMe_3$, SMe, BR_2, SiR_3, Ph, vinyl;
ii. the boron compounds are directly bonded to sp^2 or sp carbons;
iii. or, OR or OH groups are bonded to the boron atom.

A summary of typical ^{11}B NMR chemical shifts all relative to the standard BF_3-OEt_2 is shown in Table 2.2.[107].

Table 1.2: Summary of typical ^{11}B Chemical Shifts.[107]



In order to analyse the sample using ^{11}B NMR spectroscopy, it is required that the sample be placed in a quartz NMR tube not a glass NMR tube, this is due to the fact that the normal borosilicate tubes have a high level of boron in the glass and thus resonates as a very broad band, consequently, interferes with sample signals.

2.2 Gas Chromatography-Mass Spectrometry (GC-MS)

2.2.1 Introduction

GC-MS is without doubt the most widely used analytical technique for the analysis of complex mixtures. It is often said to be the most successful of all the hyphenated techniques[108] and is likened to a good marriage, as both components bring something unique into their union.[109] Gas chromatography is readily able to separate volatile and semi volatile compounds in a mixture based on their different affinities for the stationary phase on the column, however it is not able to identify the individual components. On the other hand, the mass spectrometer is able to detect and quantify the various species eluting off the column and can also provide detailed structural information in such a way that they can be definitively identified.

GC-MS was developed in early 1950s, shortly after the development of GC.[109] The combination of these two techniques was a greater success due to the fact that these techniques are, in many ways complementary to each other.[109] In this technique, the mixture is initially vaporised and then allowed to travel through a column typically coated with silica, during which separation takes place and the individual components are allowed to pass into the mass spectrometer where it is analysed. A schematic diagram of a GC/MS system is shown in Figure 2.12. The following sections provide a more detailed explanation of each component involved in this process.

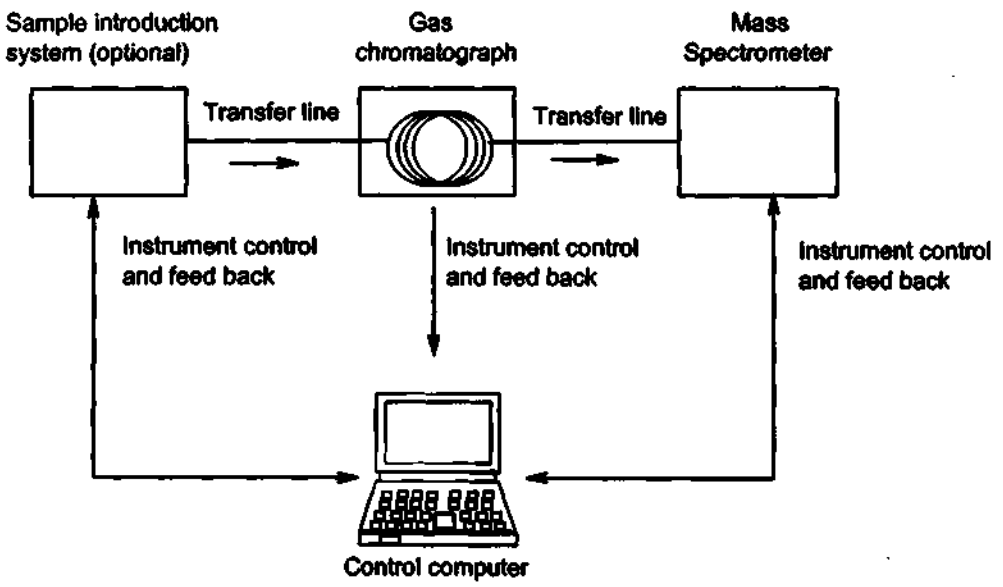


Figure 2.12: Block diagram of a GC/MS system

2.2.2 Gas chromatography (GC)

Gas chromatography is an abbreviated name for *gas liquid chromatography*. Here the sample is vaporized when injected onto the head of a chromatographic column. The sample is carried through the column by the flow of an inert gaseous mobile phase (Figure 2.13 shows a schematic representation of a GC).[110] Chemically inert gases such as helium, argon, nitrogen, carbon dioxide and hydrogen are typically used, helium being the most common. A microsyringe is used to inject a sample through a septum into a flash vaporizer port found at the head of the column.

There are two types of columns that are normally employed in GC, open tubular or capillary and packed column. Open tubular columns are superior to packed columns because they are faster and more efficient.[110] Most columns are made of glass, steel, fused silica, or Teflon®. Their lengths range from less than 2 m to 50 m or more. The column is located in the oven with a thermostat in order to set the oven to the required temperature. The degree of separation needed together with the boiling point of the sample determine the optimum column temperature/s. In order to get reasonable elution times (*ca.* 2 min to

30 min), the oven temperature must be set equal to or slightly above the boiling point of a sample. Temperature programming is used for analysis of samples with broad boiling range; here the column temperature is elevated continuously or in steps as the separation proceeds.[110]

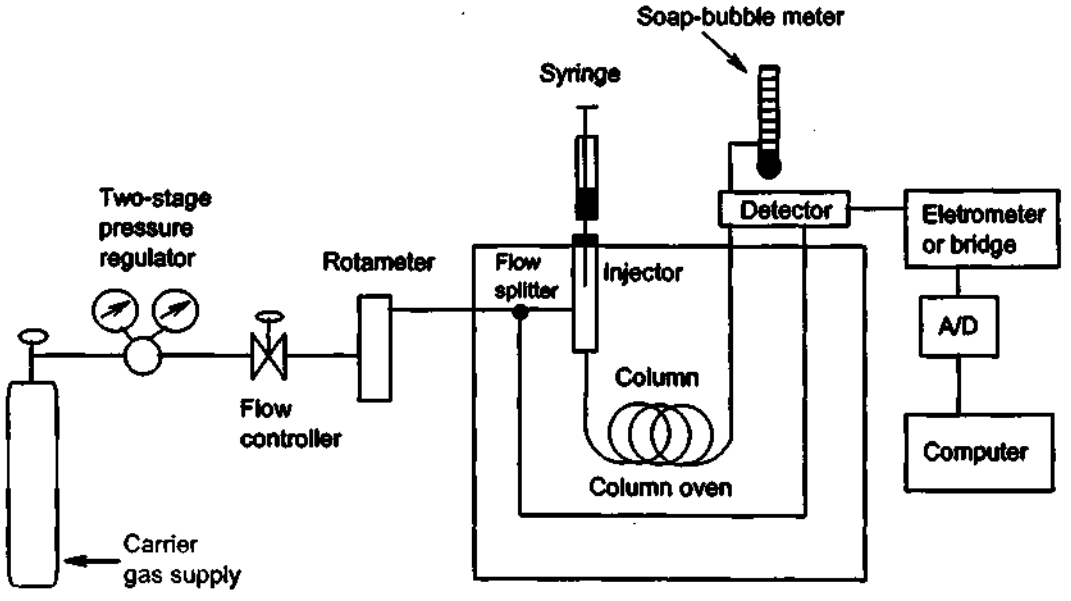


Figure 2.13: Schematic representation of a gas chromatograph.[110]

In most GCs, detection of the separated components leaving the column is performed by a flame ionization detector (FID) (Figure 2.14). This method of detection involves electrical ignition of a mixture of the effluent from the column, hydrogen gas and air. Most organic compounds are pyrolyzed during this process and they produce ions and electrons that can conduct electricity through the flame.[110]

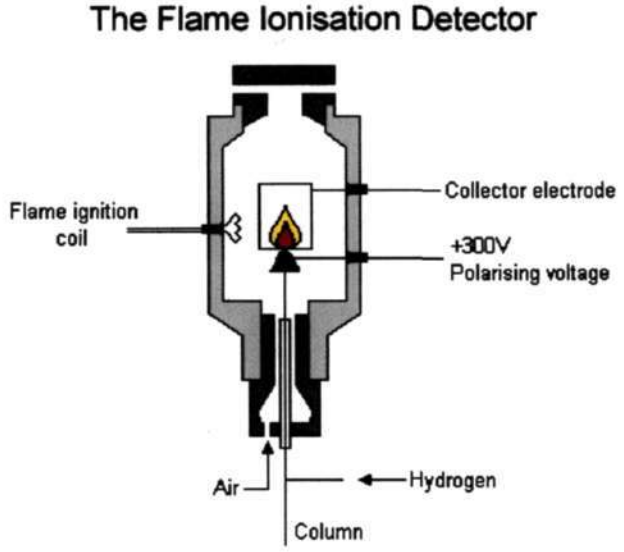


Figure 2.14 Schematic representation of the flame ionisation detector (FID)[110]

The produced ions and electrons are passed through an electrode with a voltage differential across the terminals, thus any resultant current from these electrons is able to be measured by a high-impedance operational amplifier. A disadvantage of this detector is that it destroys the sample. As mentioned in the introductory section, GC is often coupled with a selective technique of spectrometry resulting in the so-called *hyphenated method*, GC-MS.[110] This means that instead of passing the separated components from the column to the FID or any other detector, the components are allowed to directly enter the mass spectrometer for analysis.

2.2.3 Mass spectrometry (MS)

Mass spectrometry has developed dramatically over the years and a wide variety of instruments are available with different advantages or applications from each other. Some of these techniques include time-of-flight, ion-trap and quadrupole. A brief introduction to this technique will be given, to illustrate the underlying concepts involved.

In mass spectrometry, sample components are allowed to enter the MS whilst they are still in gaseous phase. They are then bombarded with an electron beam of high energy (*ca.* 70 electron volts). This bombardment knocks electrons off the molecules, producing positively charged ions known as the parent or molecular ion (Equation 4.2).[111] Molecular ions are also called radical cations as they contain a positive charge and an odd number of electrons, making them free radicals.

$$M + e^- \longrightarrow M^{\bullet+} + 2e^-$$

M = molecule
e^- = high-energy electron
$M^{\bullet+}$ = molecular ion

Equation 4.2

The electron beam gives molecular ions excess energy (70 eV ~ 1600 kcal mol^{-1}) which is more than the energy needed to break covalent bonds (50 - 100 kcal mol^{-1}),[111] as a result the parent molecular ions tend to fragment as soon as they are formed. Fragmentation leads to a number of new cations. This fragmentation is very important since it gives useful information about the structure of the molecule under investigation as these fragmentations tend to follow predictable patterns, which provide useful structural information. For example, if the sample under investigation were ammonia, the following fragmentation is observed (Equation 5.2).[111]

$$NH_3 + e^- \rightarrow [NH_3]^{\bullet+} + 2e^-$$

$$[NH_3]^{\bullet+} \rightarrow [NH_2]^+ + H$$

$$[NH_2]^+ \rightarrow [NH]^{\bullet+} + H$$

$$[NH]^{\bullet+} \rightarrow [N]^+ + H$$

Equation 5.2

The cations produced during fragmentation are sorted according to their mass to charge (*m/z*) ratio, this is achieved by accelerating the ions through a series of plates. Electric forces shape these ions into a beam that passes between poles of a magnet (Figure 2.15).[112] The magnetic field deflects this beam to form a curved path. The curvature of the path depends on the mass to charge ratio of the ion. The smaller ions in the sample are deflected most while the larger ions are deflected the least.[112] As the positively charged ions reach the detector assembly, they are separated according to their mass to charge ratios. The MS then displays a graph of a series of peaks of varying intensity as a function of mass to charge ratios.

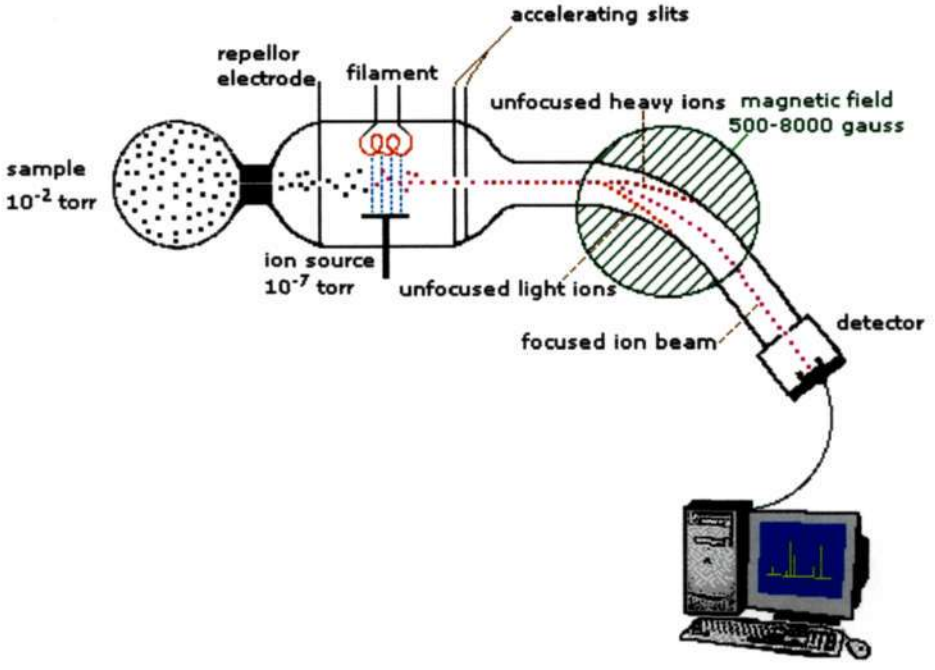


Figure 2.15: A schematic diagram of a mass spectrometer.[98]

Another analytical system that has been developed over the last decade is the ion trap mass spectrometer. An ion trap mass spectrometer uses three electrodes to trap ions in a

small volume. These ions are analyzed from a mass analyzer consisting of a ring electrode separating two hemispherical electrodes. Ions are ejected from the trap by changing the electrode voltages. As a result, a mass spectrum is obtained.[113] The advantages of the ion trap mass spectrometer are:

1. It has a compact size
2. The ability to trap and accumulate ions to increase the signal-to-noise ratio of a measurement.
3. High sensitivity

This makes the ion trap an extremely versatile and low-priced mass spectrometer, this technique is attractive to apply to analysis of biological and biochemical problems.[114]

Chapter 3.

Discussion

3. DISCUSSION

3.1 Introduction

The value and widespread applicability of α-olefins (as discussed in Chapter 1 sections 1.1 and 1.2) motivated the investigations into the possible contrathermodynamic isomerization of alkenes (Section 1.5.3), as it has been demonstrated[45] that the hydroboration reaction will play a pivotal part in our approach to a contrathermodynamic isomerization cycle. Brown has studied this key reaction in great detail over the past few decades.[7, 8, and 9] Other members within our team have conducted studies on hydroboration reactions using BH_3, haloborane derivatives, borane dimers, and boranes coordinated to different types of Lewis bases in order to obtain kinetic and thermodynamic data for this process.[115, 116, and 117]

To date, four research students are currently involved in the Sasol National Double Bond Isomerization project. The first student A. B. Mzinyati,[115] conducted a study of hydroboration of acrylonitrile, allyl cyanide and acetonitrile with borane-dimethyl sulfide complex. These reactions demonstrated that ^{11}B NMR spectroscopy can be used to monitor the kinetics of hydroboration *in situ*.[115] In this study it was found that acrylonitrile was reduced at the nitrile functional group at 30 °C at a rate of $(7.69 \pm 0.20) \times 10^{-4}$ $M^{-1}s^{-1}$, it was also found that allyl cyanide was hydroborated at the alkene functional group at a rate of $(2.24 \pm 0.20) \times 10^{-3}$ $M^{-1}s^{-1}$ whilst no reduction of the nitrile group was observed for acetonitrile at 30 °C. A temperature dependence study for the hydroboration of acrylonitrile to vinyl iminoborane was conducted, the values of enthalpy and entropy of formation from depletion of BH_3:SMe_2 and formation of vinyl iminoborane were determined.[115]

The second student J. R. Govender, conducted a study of the mechanism and kinetics of hydroboration of 1- and 4-octene using dimeric diakylboranes and BH_3:SMe_2 complex as the source of borane.[116] Diisopinocamphenylborane, dicyclohexylborane and (3,6-dimethyl)borepane were used for the hydroboration of 1- and 4-octene, and it was found

from the observed rate constants (k_{obs}) that these reagents hydroborate 4-octene at a slower rate than 1-octene.[116]

Using the observed rate constants for the hydroboration of 1-octene, the following trend of hydroboration was determined:- BH_3:SMe_2 > dicyclohexylborane > diisopinocamphenylborane > (3,6-dimethyl)borepane.[116] This trend was attributed to the steric hindrance afforded by the bulky cyclohexyl and diisopinocamphenyl groups. These results were also supported by computational studies. It was also found that the mechanism for the hydroboration of 1-octene with dimeric boranes follows 3/2-order kinetics. This indicated that the rate determining step was the dissociation of the dimer, followed by the reaction of the monomeric borane with the alkene.[116]

The third research student N. Xaba,[117] conducted hydroboration of 1-octene with $HBBr_2$:SMe_2 and H_2BBr:SMe_2 complexes. Displacement reactions of the octyl-bromoborane by 1-hexyne, acrylonitrile and allyl cyanide were also investigated using GC to monitor the progress of the reaction. In this study, a comparison between kinetic data obtained from GC and ^{11}B NMR spectroscopy was carried out, in which it was clearly shown that ^{11}B NMR spectroscopy was considerably superior to GC.[117]

A competitive study also showed that $HBBr_2$ hydroborates 1-octene 2.5 fold faster than acrylonitrile and 13 fold faster than allyl cyanide, while on the other hand it was found that H_2BBr hydroborates 1-octene 5 fold faster than acrylonitrile and 66 fold faster than allyl cyanide.[117]

From the studies conducted within our group and from the literature it is evident that the kinetics of hydroboration is indeed complex, due to the potential number of possible reactions the boron group is able to undergo. Borane has three sites available for hydroboration, as a result the overall process involves three addition reactions (Equation 1.3), five monomer dimer equilibria (Equation 2.3), and three redistribution equilibria (Equation 3.3).[97]

Another problem associated with BH_3 hydroboration is that the reactions are too fast to be measured accurately using ^{11}B NMR spectroscopy.

$$\text{Alkene} + BH_3 \rightarrow RBH_2$$
$$\text{Alkene} + RBH_2 \rightarrow R_2BH$$
$$\text{Alkene} + R_2BH \rightarrow R_3B$$

Equation 1.3

$$BH_3 + RBH_2 \Leftrightarrow H_2BH_2BHR$$
$$BH_3 + R_2BH \Leftrightarrow H_2BH_2BR_2$$
$$2RBH_2 \Leftrightarrow RHBH_2BHR$$
$$RBH_2 + R_2BH \Leftrightarrow RHBH_2BR_3$$
$$2R_2BH \Leftrightarrow R_2BH_2BR_2$$

Equation 2.3

$$BH_3 + R_3B \Leftrightarrow RBH_2 + R_2BH$$
$$2RBH_2 \Leftrightarrow R_2BH + BH_3$$
$$2R_2BH \Leftrightarrow R_3B + RBH_2$$

Equation 3.3

Consequently, it was decided to limit the focus of this study to single site boron compounds (which would avoid the difficulties illustrated in equations 3.1, 3.2 and 3.3) with the aim of being able to study their potential for contrathermodynamic isomerisation of alkenes. In addition we decided to focus our attention on the use of heteroatom containing boron compounds, in order to evaluate the role of the heteroatoms on hydroboration, isomerisation and ultimately displacement.

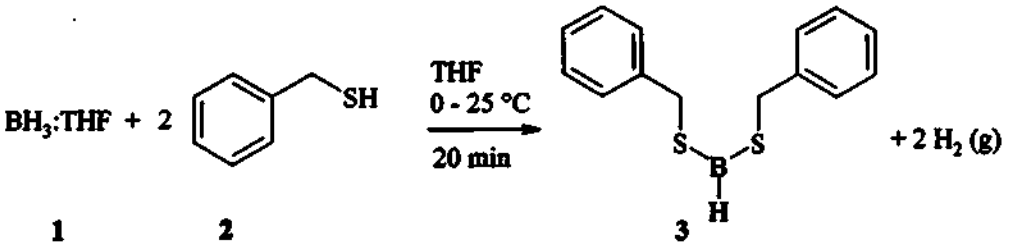
In this study we intend to investigate the role sulfur, nitrogen and oxygen heteroatoms play in the reactivity of these hydroboration reactions. In the literature there have been very few publications on the use of heteroatoms such as sulfur[53] and nitrogen.

Based on these observations it was hoped that by making use of these heteroatoms we would be able to slow down the reaction, thus enable us to better investigate the reaction with NMR spectroscopy.

3.2 Preparation of Alkylthioboranes (Sulfur-Based Boranes)

3.2.1 Synthesis of Bis(benzylthio)borane

The synthesis of bis(benzylthio)borane was our first attempt at the synthesis of the di-substituted sulfur-based boranes. It was synthesized using borane-tetrahydrofuran complex and benzyl mercaptan in a 1:2 stoichiometric ratio, using THF as the reaction solvent. Evolution of hydrogen gas was observed and used to monitor the progress of the reaction.



Scheme 49

Bis(benzylthio)borane (3) (Scheme 49) was obtained as a clear liquid which was then characterized by ^{11}B NMR spectroscopy. A doublet was observed at -8.3 ppm corresponding to B-H signal (Figure 3.1).

However, compounds synthesized using borane-tetrahydrofuran complex in THF were oxidized rapidly even when handled with great care under a dry nitrogen atmosphere. In fact, on some occasions the complex was oxidized prior to any reaction taking place. Due to these difficulties, it was decided to make use of the more stable borane-dimethylsulfide

complex as opposed to borane-tetrahydrofuran. This complex has been shown to be significantly more stable[28, 29]

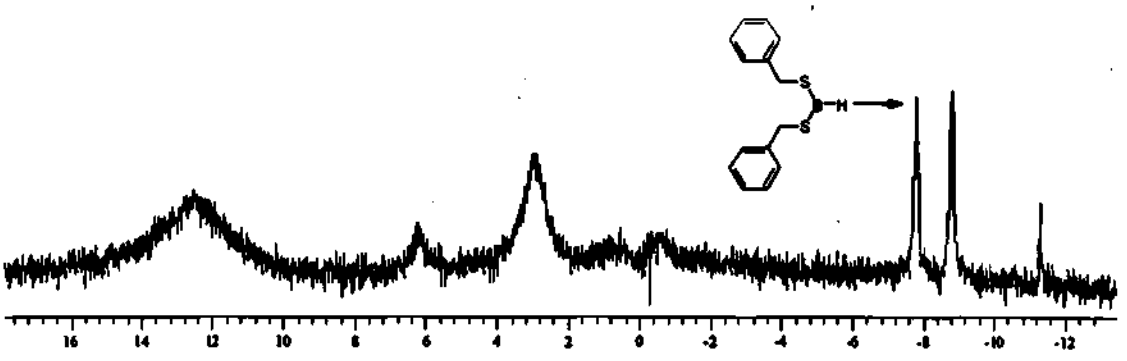


Figure 3.1 ^{11}B NMR spectrum* of bis(benzylthio)borane in THF

A mixture of BH_3:SMe_2 and benzyl mercaptan in a 1:2 stoichiometric ratio were stirred for 16 hours, while warming up from 0 – 25 °C, ^{11}B NMR spectroscopic analysis of the resulting clear liquid indicated a large and intense singlet at -14.5 ppm relative to the external standard BF_3:OEt_2 (Figure 3.2). This singlet was attributed to benzylthioborane and not bis(benzylthio)borane. Pasto *et al.*[61] reported that benzylthioborane exists as a polymeric species with a polymer back-bone consisting of the $-BH_2$-SR- units. The unresolved nature of the absorption signals of this compound is due to the superimposition of the resonance lines of the boron atoms in slightly varying chemical environments in a polymer chain.[61] At 62.0 ppm a very weak doublet was observed, it was tentatively assigned as the product peak due to the observed coupling constant ($J_{B\text{-}H}$ = 178.4 Hz) which corresponds to coupling between the boron and hydrogen atoms.[104] It was hoped that maintaining the reaction temperature at 40 °C would allow the reaction from benzylthioborane to bis(benzylthio)borane to take place. After 2 hours, the same mixture showed only a broad singlet at 59.1 ppm (Figure 3.3). The sample was then mixed with an alkene (1-octene) in order to establish its identity. After several hours of boiling, the mixture afforded no product, indicating that there was no site available for hydroboration. Consequently this peak was attributed to the formation of the unreactive and stable tribenzylthioborate.

* All ^{11}B NMR spectra, unless indicated are coupled spectra, indicating boron-proton coupling, and are scaled in parts per million (ppm).

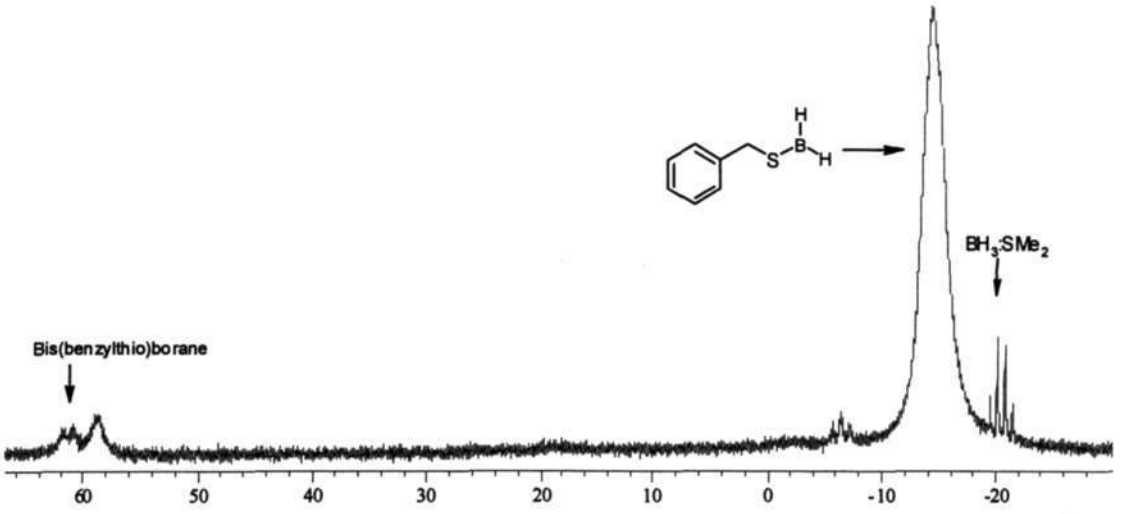


Figure 3.2 ^{11}B NMR spectrum of the product mixture obtained using BH_3:SMe_2 with benzyl mercaptan

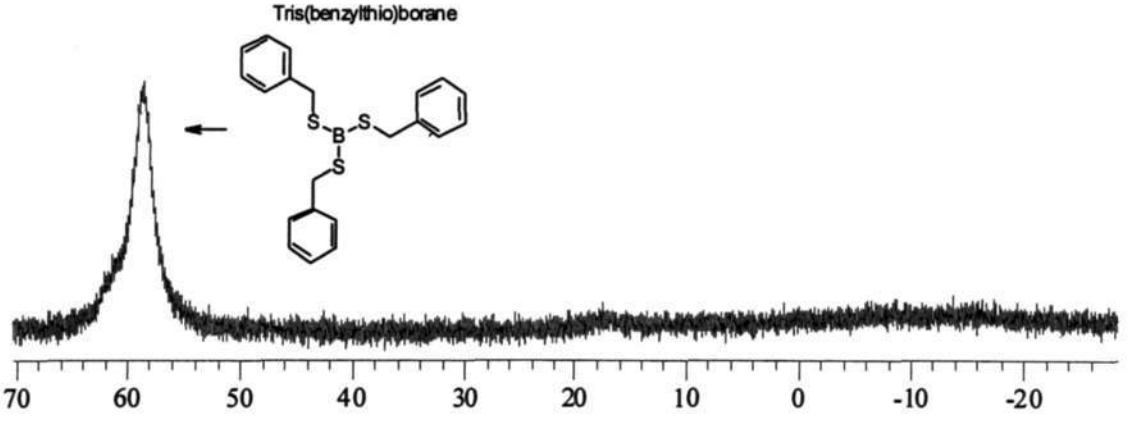
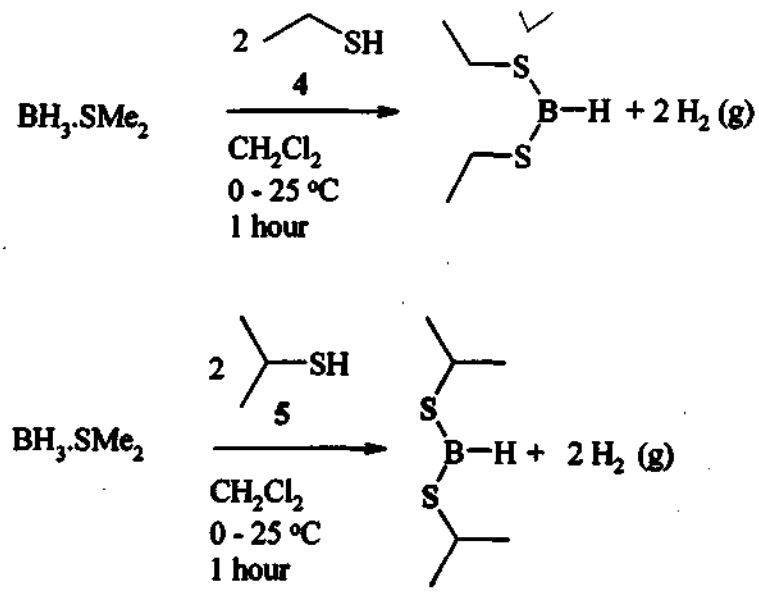


Figure 3.3 ^{11} B NMR obtained after keeping the reaction in Scheme 49 at 40 °C for 2 hour

In a publication by Pasto *et al.*[61] it was reported that one is able to obtain the desired product bis(phenylthio)borane in sufficiently high yields by reacting the tris(phenylthio)borane species with BH_3:THF. On evaluation of this it was decided that this would not in fact be a suitable synthetic path as it appeared likely that one would have a distribution of excess BH_3, the trimer, and the desired product. Separation of these species was also not seen as a viable option.

3.2.2 Synthesis of Bis(isopropylthio)- and (ethylthio)boranes

In this reaction, 2 molar equivalents of ethyl mercaptan (**4**) (Scheme 50) were reacted with 1 molar equivalent of $BH_3.SMe_2$ in CH_2Cl_2. This reaction afforded however, polymeric alkylthioboranes. In a similar reaction with isopropyl mercaptan (**5**) (Scheme 50), with 1 molar equivalent of $BH_3.SMe_2$ in CH_2Cl_2 the same observations were made. These products were characterized using ^{11}B NMR spectroscopy.



Scheme 50

A broad triplet at –15.8 ppm (Figure 3.4) was observed in the ^{11}B NMR spectrum of the product mixture, this was assigned to the isopropylborane trimer. Sheludyakova *et al.*[63] obtained polymeric alkylthioboranes from the reaction of ethyl and butyl mercaptans with diborane in diethyl ether. These results are consistent with this work.

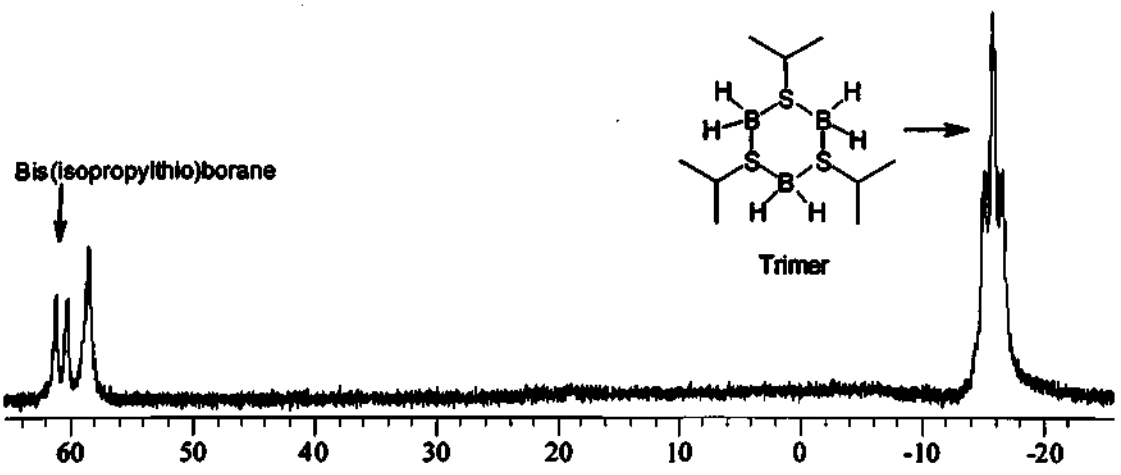
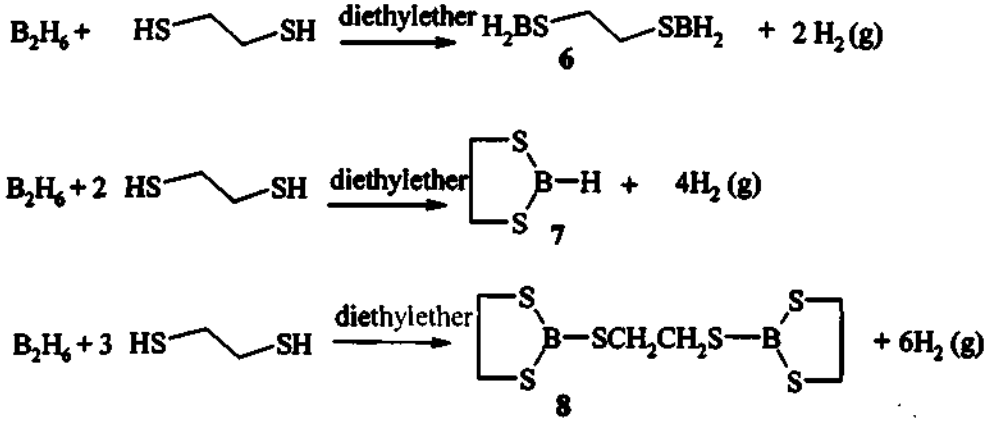


Figure 3.4 ^{11}B NMR spectrum of the product mixture, showing the structure of trimeric species obtained from the reaction of isopropyl mercaptan with BH_3:SMe_2

3.2.3 Synthesis of 1,3,2-Dithiaborolane

Egan *at al.*[118] showed that heterocyclic derivatives of alkythioboranes can be synthesized from diborane and 1,2-ethanedithiol. This reaction is dependent upon the stoichiometric ratios of the reactants.



Scheme 51

Compounds (6), (7), and (8) (Scheme 51) have very different properties from their analogues derived from 1,2-ethanediol and diborane.[118] 1,2-ethanediol derivatives are

viscous, glassy substances while the ethanedithiol derivates are crystalline solids at room temperature. 1,3,2-Dithiaborolane (7) (Scheme 51) has been heated to 90 °C without significant disproportionation into B_2H_6 and $(CH_2S)_2BSCH_2CH_2SB(CH_2S)_2$ while on the other hand, its analogue $(CH_2O)_2BH$ undergoes disproportionation at room temperature.[118] Molecular weight measurements and examination of solid and vapour infrared spectra showed that 1,3,2-dithiaborolane is a monomer in the gas phase. These observations suggest that in the condensed state, quaternization of boron occurs through intermolecular coordinate bonds between boron and sulfur. Possible species are shown in Figure 3.5.

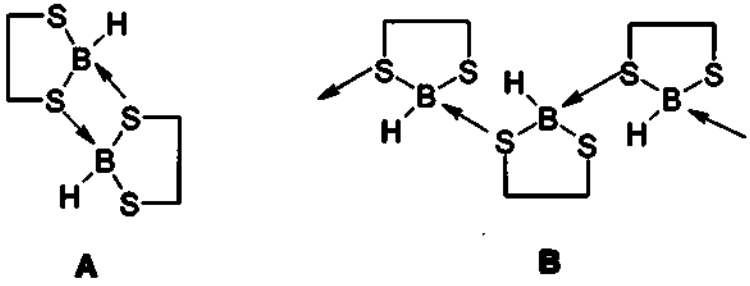


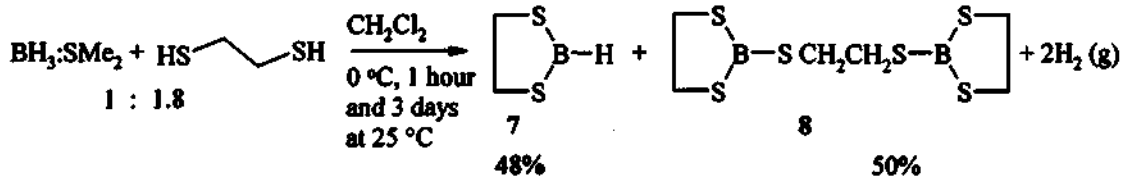
Figure 3.5

Its physical properties show that it can exist in a more than one associated form in the solid state, and its liquid form at room temperature might be a low molecular weight which on standing very slowly polymerizes to form a higher molecular weight solid.

During studies in our laboratory on the synthesis and characterization of heterocyclic derivatives of alkythioboranes, it was found that not only the desired compound, that is, 1,3,2-dithiaborolane (7) was produced as proposed by Egan *et al.*[118], but in fact, a mixture of two products (Figure 3.6) about 55% of 1,3,2-dithiaboronane, 41% of 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8) and 4% unreacted BH_3:SMe_2. Studies were then conducted to explore the factors that influence this distribution.

Firstly BH_3:SMe_2 was allowed to react with 1.8 equivalents of 1,2-ethanedithiol at 0 °C. ^{11}B NMR analysis showed a small amount of unreacted BH_3. SMe_2 and a doublet at 60.5

ppm (Figure 3.6) corresponding to 1,3,2-dithiaborolane (7) (Scheme 52). A low yield of about 48% was found. A singlet at 64.0 ppm which was attributed to 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8) (Scheme 51) with a 50% yield.



Scheme 52

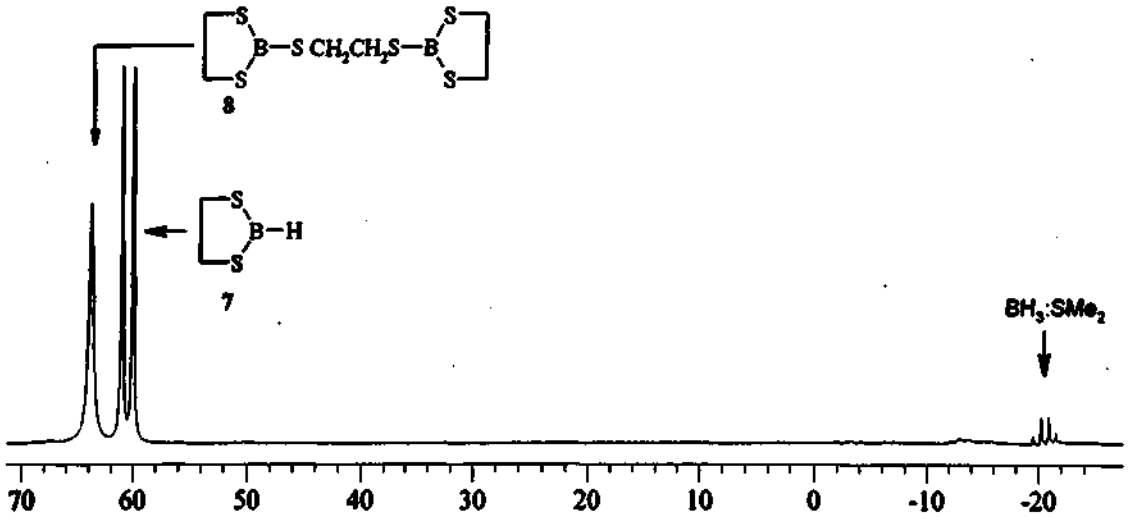


Figure 3.6 ^{11}B NMR spectrum, showing the products obtained in the reaction of 1,2-ethanedithiol with BH_3:SMe_2.

The same reaction was conducted at -80 °C and allowed to warm up to room temperature for 15 minutes. It was found that the percentage yield of 1,3,2-dithiaborolane (7) had increased to approximately 50% of the total mixture.

When, the above stoichiometric ratio was changed to 1.5 moles* of BH_3SMe_2 : 1 mole of 1,2-ethanedithiol, with the reaction temperature at -84 °C and allowed to slowly warm to room temperature over a period of 2 days, a high yield of 71% of 1,3,2-dithiaborolane (7) was obtained; 11% unreacted BH_3 and 18% of 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) made up the remainder of the composition. Changing the stoichiometric ratio to 1.25 : 1 by slowly increasing the amount of mercaptan at the same temperature and conditions, reduced the yield of (7) to 64%. Increasing the amount of mercaptan to afford a 1.04 : 1 molar ratio gave a low yield of 45% of (7) and 52% of 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane).

Interesting observations were found in a reaction of a 1:1 mole ratio of BH_3 and mercaptan at -75 °C for 1.5 hour and 4 days at room temperature. 55% of (7) and 41% of 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8).

Thirdly, it was of interest to check if keeping the reaction mixture at low temperature for a longer period would have any effect on the yield of (7).

BH_3 was allowed to react with an equimolar amount of 1,2 ethanedithiol at -84 °C for 30 minutes and at -55 °C for 2 days gave 65% of (7), 17% of 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) and 18% of unreacted BH_3. After 14 days it was found that there was only 2% of unreacted BH_3 remaining, (7) had gone down to 58% and 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) to 40%. The lower percentage of BH_3 was acceptable because it reduces the possible competition between BH_3 and 1,3,2-dithiaborolane towards the alkene on hydroboration. This synthetic approach was chosen to be the best for the synthesis of 1,3,2-dithiaborolane. These findings are best summarized in Table 3.1. These results indicate that there is a kinetic thermodynamic equilibrium that has been established with 1,3,2-dithiaborolane (7) being the thermodynamic product. From these results we are able to increase the amount of desired

* The goal was to optimize the yield of (7) with as little unreacted BH_3:SMe_2 as possible, hence this mole ratio was not repeated.

product for later studies, and the reaction by product (8) is unreactive and hence will play no part in our further studies.

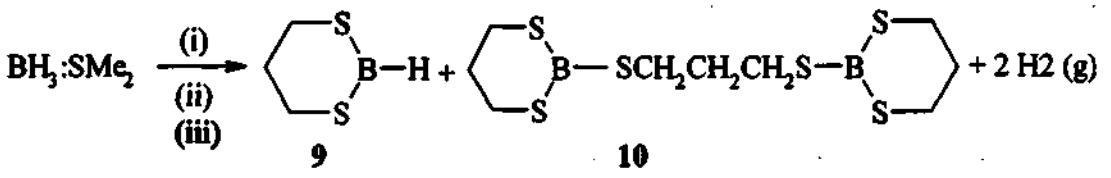
Table 3.1 Summary of results obtained in the synthesis of 1,3,2-dithiaborolane.

No.	Time (hours)	Temp (°C)	Stoichiometric Ratio		Product (7) %	By-Product (8) %	BH_3 %
			BH_3 (mol)	1,2-ethanedithiol (mol)			
1	1	0	1	1.8	48	50	2
2	1	-80	1	1.8	50	46	4
3	1	-84	1.5	1	71	18	11
4	1	-84	1.25	1	64	29	16
5	1	-84	1.04	1	45	52	3
6	1.5	-84	1	1	55	41	4
7	48	-84 to -55	1	1	65	17	18
8	336	-84 to -55	1	1	58	40	2

3.2.4 Synthesis of 1,3,2-Dithiaborinane

A synthetic procedure proposed by O'Neill *et al.*[68] was used. In this method, borane-dimethyl sulfide complex reacted with an equimolar amount of 1,3-propanedithiol in CH_2Cl_2 at 0 °C and was stirred for a week at 25 °C. The resulting milky liquid exhibited a ^{11}B NMR spectrum with a doublet at 55.4 ppm (Figure 3.7),which was attributed to the reagent 1,3,2-dithiaborinane (9) (35% yield). A singlet was also observed in the same mixture at 56.6 ppm and this was the major product of the reaction (*ca.* 55% yield) and this was attributed to the disproportionation product 2,2′-(propylenedithio)-(1,3,2-dithiaborinane) (10) (Scheme 53). A triplet at 16.9 ppm was attributed to a mono-substituted borane fragment (7% yield), some unreacted BH_3:SMe_2 (3% yield) was also shown as a quartet at -20.0 ppm. These yields were low when compared to the minimum yield of 48% obtained in the previous study. The optimum synthetic method designed for

1,3,2-dithiaborolane was employed in this situation in order to achieve better yields. However, no yield elevation for 1,3,2-dithiaborinane was achieved, and a maximum yield of 34% of the product was obtained in this case.



(i) CH_2Cl_2
(ii) 2 equivalents of 1,3 propanedithiol,
(iii) 0 °C 1 hour and 3 days at 25 °C

Scheme 53

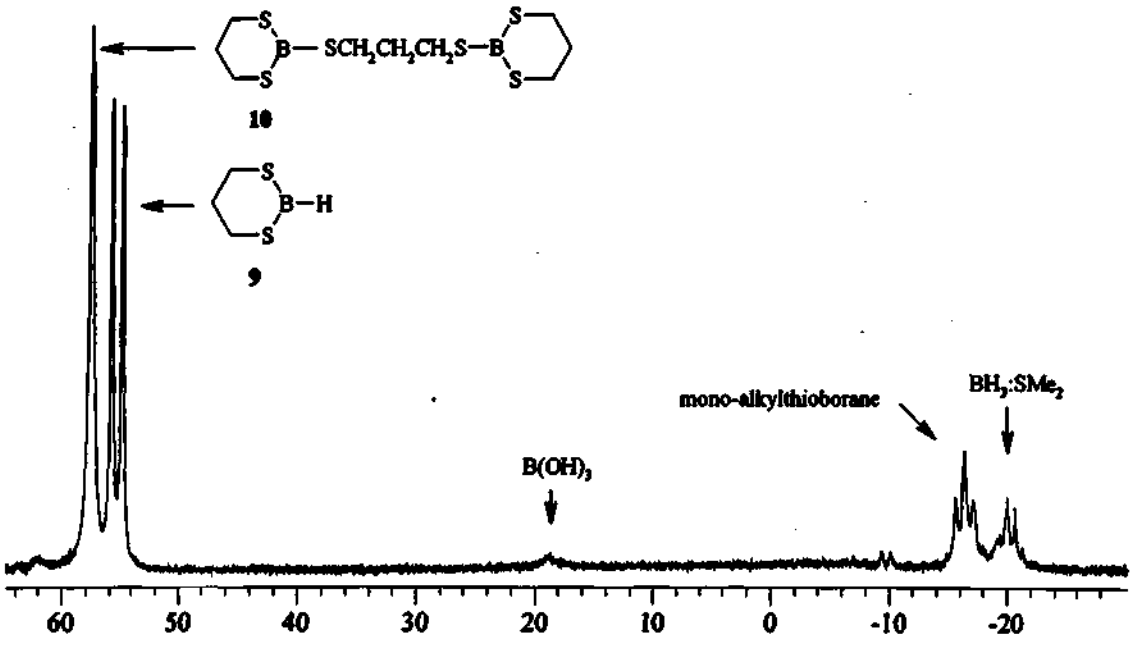


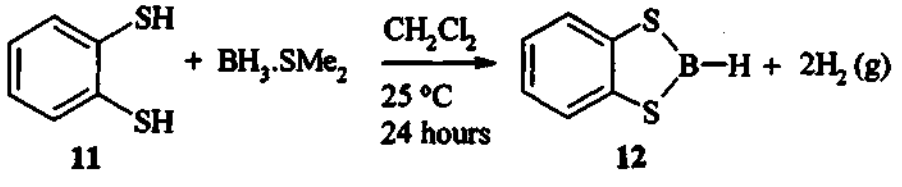
Figure 3.7 ^{11}B NMR showing the obtained fragments in the reaction of 1,3-propanedithiol with borane-dimethyl sulfide complex

It was found that these alkylthioboranes (compounds 7 and 9) are highly sensitive to air, moisture and elevated temperatures. Upon exposure to moisture these compounds are

oxidised - this effectively means that the B-H bond breaks and a B-OH bond forms due to attack by an hydroxide into the empty p_z-orbital on the boron. After oxidation, these products are not useful in hydroboration reactions. At elevated temperatures, these reagents disproportionate to (8) and (10) respectively. Therefore, it was of prime importance that these reagents be kept under inert atmosphere and low temperature (for this research, the reagents were kept in the freezer at -20 °C and under an atmosphere of dry nitrogen in order to minimize disproportionation and oxidation).

3.2.5 Synthesis of Benzo-1,3,2-dithiaborolane

Most of the reagents prepared in the preceding sections required laborious techniques to force the reactions to yield the desired compounds in sufficiently high yield. However, the aromatic derivative of 1,3,2-dithiaborolane is easily prepared from the reaction of equimolar amounts of 1,2-benzenedithiol (11) and borane-dimethyl sulfide complex in CH_2Cl_2 at room temperature under an atmosphere of dry nitrogen (Scheme 54). The reaction was found to be slow and mild with no observable effervescence at room temperature.



11 12

Scheme 54

^{11}B NMR analysis (Figure 3.8) obtained after stirring the mixture for 24 hours at 25 °C showed a clean spectrum with only a doublet at 53.4 ppm attributed to a B-H coupling signal of benzo-1,3,2-dithiaborolane (12) (Scheme 54). It can also be seen from this spectrum that there was no remaining unreacted BH_3:SMe_2 complex. The proton decoupled spectrum of the sample (Figure 3.9) showed only a singlet at 53.4 ppm due to the boron atom in (12), this confirmed that the doublet was, in fact, due to B-H coupling

of the target compound (12). According to the acquired ^{11}B NMR evidence, benzo-1,3,2-dithiaborolane was synthesized selectively in quantitative yields. It was speculated that the aromatic ring play a significant role in increasing the yields of (12) in contrast to (7) (65%) and (9) (35%). The aromatic ring donates the electron density to the sulfur atoms, which in turn donate it to the boron atom. This makes the boron atom less electropositive which reduces to possibility of dimer formation.

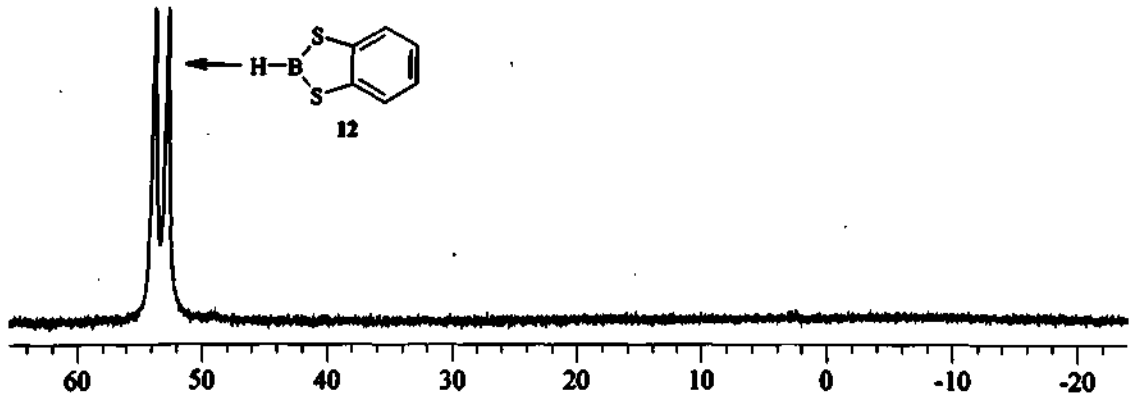


Figure 3.8 ^{11}B NMR spectrum showing a doublet of benzo-1,3,2-dithiaborolane

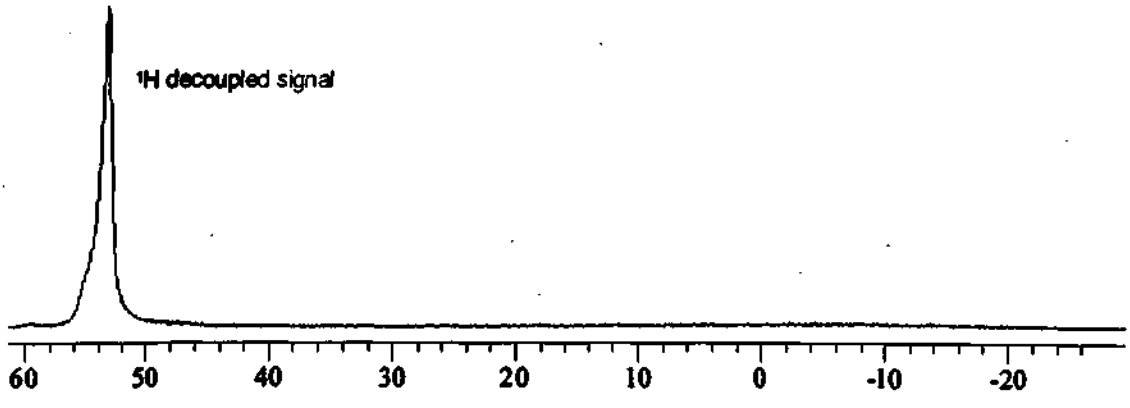
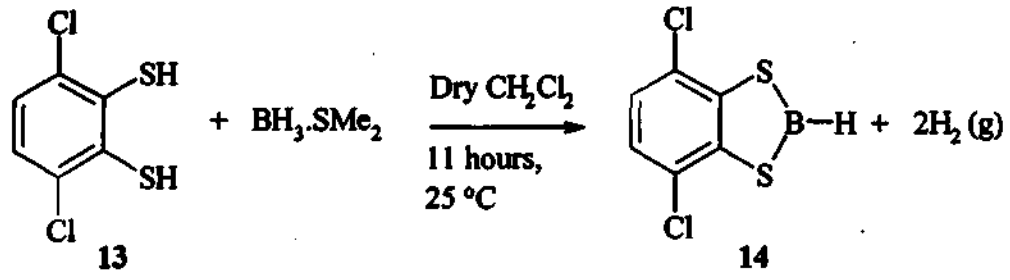


Figure 3.9 Showing a proton decoupled ^{11}B NMR spectrum of benzo-1,3,2-dithiaborolane

3.2.6 Synthesis of 4,7-Dichloro-1,3,2-benzodithiaborolane

The chlorinated derivative of benzo-1,3,2-dithiaborolane was readily synthesized from a reaction of 3,6-dichloro-1,2-benzenedithiol (13) with borane-dimethyl sulfide complex in a 1:1 stoichiometric ratio (Scheme 55). When the reaction was carried out at room temperature, no effervescence, indicative of hydrogen gas liberation, was observed. However, analysis of the resulting mixture showed a doublet at 53.2 ppm (corresponding to *ca* 17% conversion) attributed to (14) (Scheme 55) and the rest of the mixture was the unreacted BH_3:SMe_2 complex (Figure 3.10).



Scheme 55

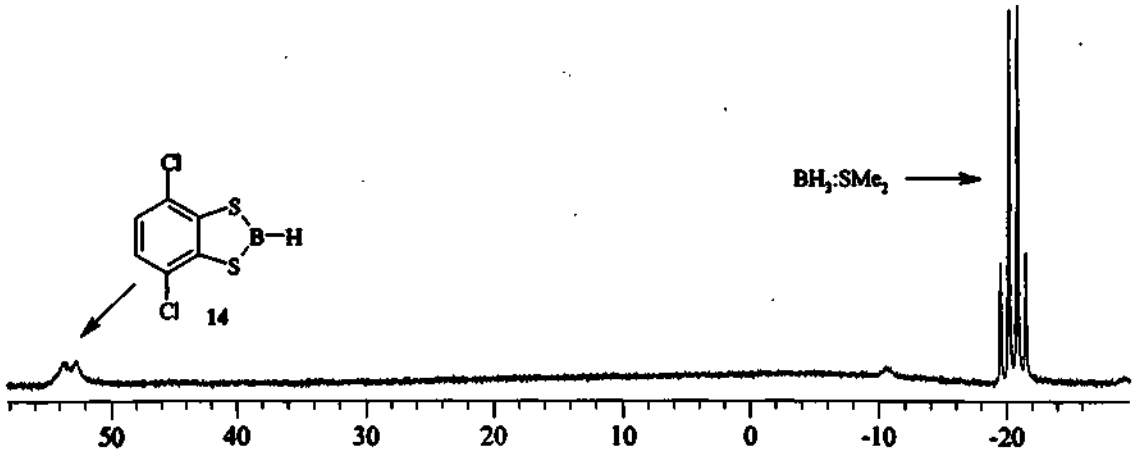


Figure 3.10 ^{11}B NMR spectrum showing the product obtained from the reaction in Scheme 55 after 11 hours at 25 °C

The mixture was refluxed in CH_2Cl_2 for 4.5 hours in order to drive the reaction to completion. An appreciable 67% yield of (**14**) was achieved after this period (Figure 3.11). The mixture was subsequently refluxed for a further 2.5 hours, and the ^{11}B NMR analysis of this mixture displayed only one doublet at 53.2 ppm (Figure 3.12). No other peaks were observed, and therefore 4,7-dichloro-1,3,2-benzodithiaborolane (**14**) compound was synthesized in quantitative yield based on the ^{11}B NMR spectrum.

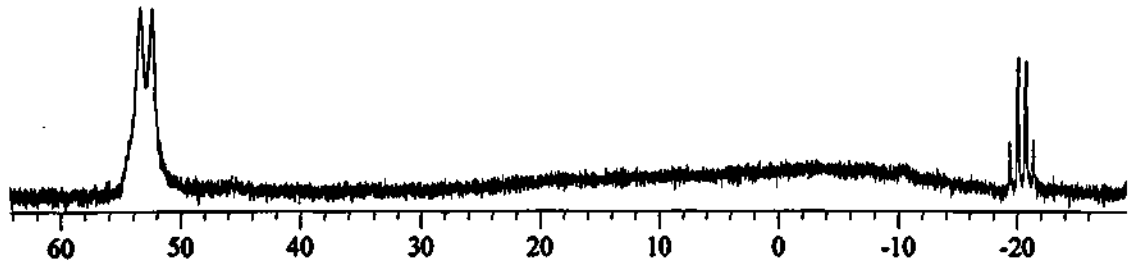


Figure 3.11 ^{11}B NMR spectrum obtained after 4.5 hours, showing about 67% yield of (**14**) formed[∞]

When comparing the synthesis of 4,7-Dichloro-benzo-1,3,2-dithiaborolane (**14**) (Scheme 55) to that of benzo-1,3,2-dithiaborolane (**12**) (Scheme 54), it can be seen that it is easy to synthesize (**12**) while on the other hand (**14**) requires higher temperatures in order to drive the reaction to completion. This reduced reactivity of (**14**) was attributed to the electron withdrawing effect of the two chlorine substituents on the aromatic ring. These chlorine atoms significantly reduce the electron density from the aromatic ring and, in turn, from the sulfur groups. As a result of this diminished electron density the interaction between the sulfur and boron atoms is reduced.

[∞] Product percentage was measure by integration of the ^{11}B NMR spectrum.

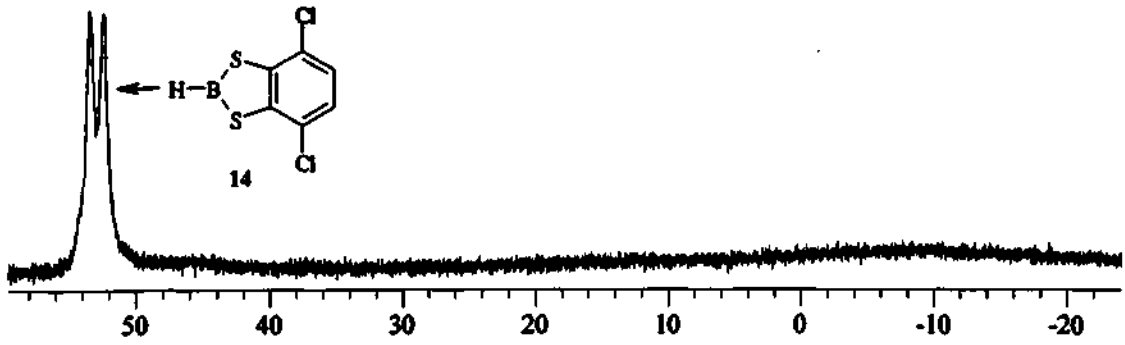


Figure 3.12 ^{11}B NMR spectrum of product (14) after 7 hours' reflux in dichloromethane.

3.3 Preparation of Alkyloxaboranes (Oxygen-Based Boranes)

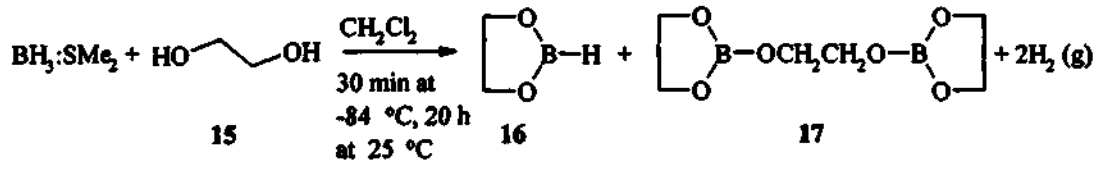
The oxygen-based derivative of benzo-1,3,2-dithiaborolane (12), that is benzo-1,3,2-dioxaborolane, also known as catecholborane (refer to Section 1.4.3.2 in Chapter 1), was introduced into the study since it was seen as a good comparison to benzo-1,3,2-dithiaborolane. This was motivated by the fact that it is commercially available in high purity. Catecholborane could be compared with (12) in terms of reactivity towards olefins because its reactivity towards olefins has been thoroughly investigated by Brown[55] and Suss.[56]

It was then decided to explore routes to synthesise an oxygen based analogue of 1,3,2-dithiaborolane (7), that is 1,3,2-dioxaborolane, in order to contrast the reactivity between the two species. The following Section discusses the preparation of 1,3,2-dioxaborolane.

3.3.1 Synthesis of 1,3,2-Dioxaborolane.

The reaction of equimolar amounts of BH_3:SMe_2 and 1,2-ethanediol at 0 °C led to the rapid evolution of hydrogen gas. Analysis using ^{11}B NMR spectroscopy showed the formation of a single product by virtue of a broad signal at 18.2 ppm. This resonance indicates the formation of $B(OH)_3$ indicating that moisture was still present.

The reaction was repeated with rigorously dried[119] and distilled 1,2-ethanediol. The reaction was conducted at -80 °C and warmed up to room temperature over a period of some 20 hours. The reaction products were characterized by ^{11}B NMR spectroscopy. A doublet at 28.4 ppm (Figure 3.13) was due to 1,3,2-dioxaborolane (**16**) (Scheme 56) and a singlet at 23.0 ppm was attributed to 2,2'-(ethylenedioxy)-bis-(1,3,2-dioxaborolane) (**17**) (Scheme 57). About 15% of 1,3,2, dioxaborolane (**16**) and 70% of the disproportionation product 2,2'-(ethylenedioxy)-bis-(1,3,2-dioxaborolane) (**17**) were obtained.



Scheme 56

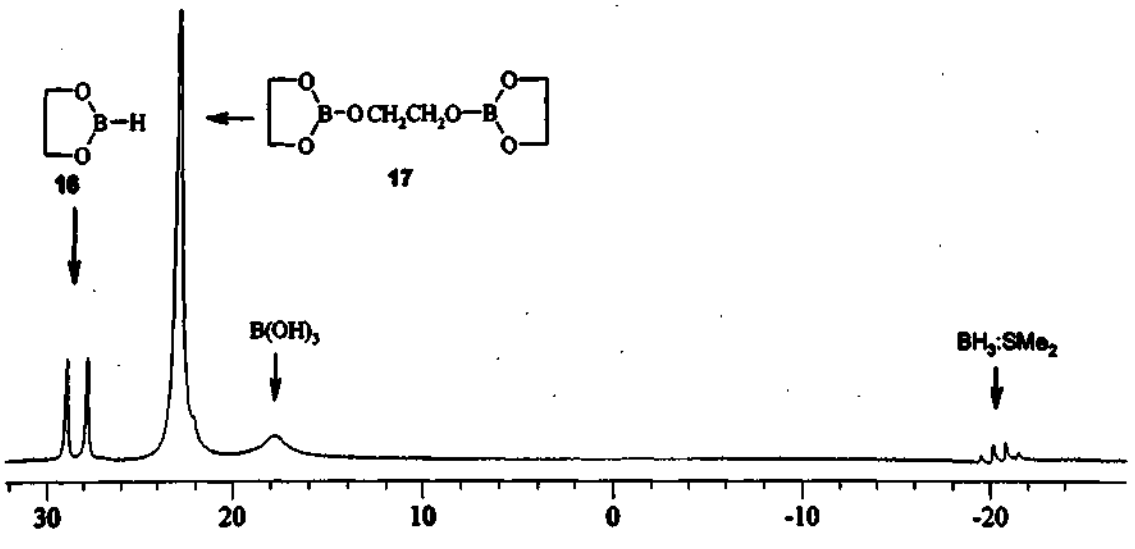


Figure 3.13 ^{11}B NMR spectrum obtained from the reaction of 1,2-ethanediol with borane-dimethyl sulfide at -84°C for 30 minutes

When the same reaction was conducted at -84 °C for 1 hour and left at -55 °C for 5 days, it was found that 1,3,2 dioxaborolane had almost completely disproportionated affording (17) in 82% yield (Figure 3.14).

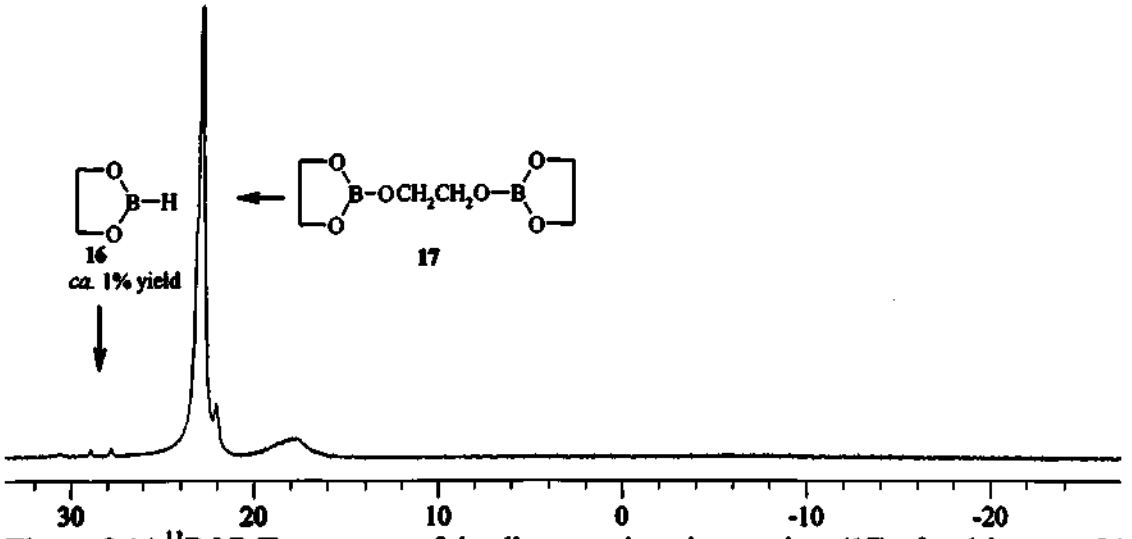
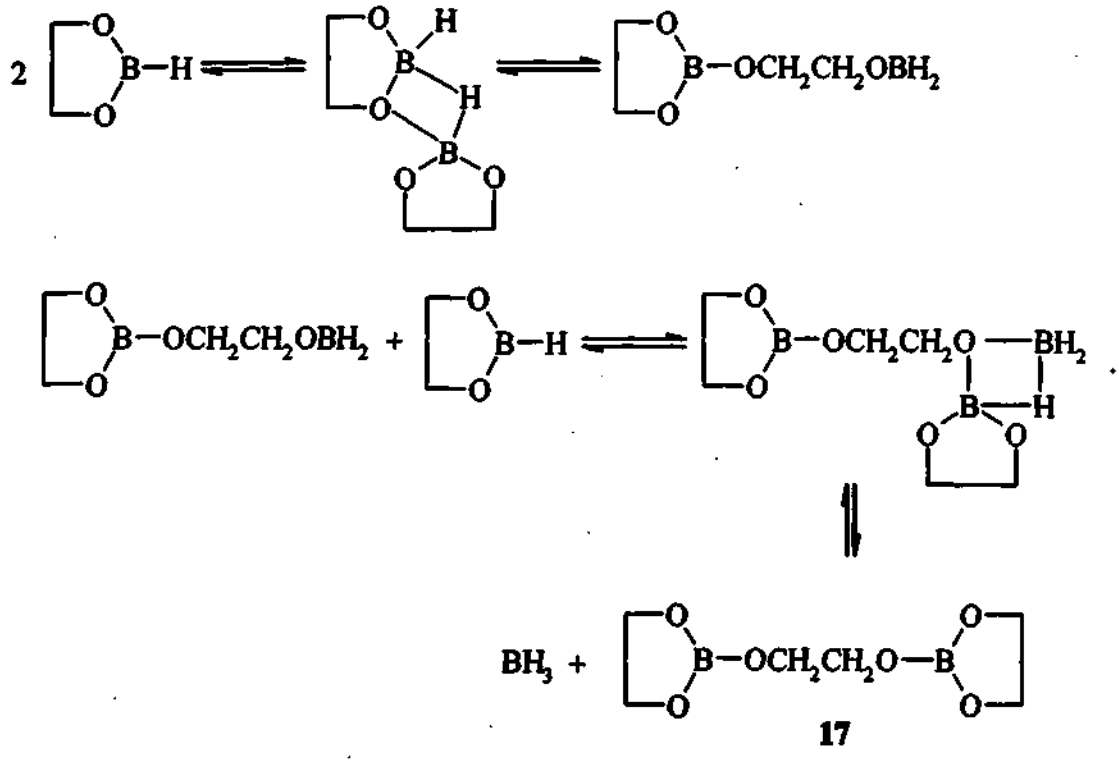


Figure 3.14 ^{11}B NMR spectrum of the disproportionation product (17) after 1 hour at -84 °C and 5 days at -55 °C

Evidence for similar disproportionation can be found in studies conducted by Rose and Shore in the early 1960's. Rose and Shore[120] synthesized 1,3,2-dioxaborolane at very low temperatures ranging from -196 to -78 °C. In their study they found that the heterocycle disproportionated in solution to form diborane and 2,2'-(ethylenedioxy)-bis-(1,3,2-dioxaborolane). THF as a reaction solvent did not minimize disproportionation. Rose *et al.*[120] obtained a stable heterocycle indirectly as a trimethyl amine adduct by binding trimethyl amine to 1,3,2-dioxaborolane at -78 °C.

In a research by Rose, a hard glassy solid was obtained as in our work. Attempts to regenerate the volatile heterocyclic from the glassy solid failed due to the fact that above 50 °C extensive disproportionation was observed. It was found that the rate of disproportionation of this compound depends upon the presence of impurities.[120] an average rate of disproportionation of 1% per minute at 25 °C was reported by Rose and

Shore.[120] A typical disproportionation proposed by Rose and Shore is shown below (Scheme 57).[120]



Scheme 57

3.4 Preparation of Alkylaminoboranes (Nitrogen-Based Boranes)

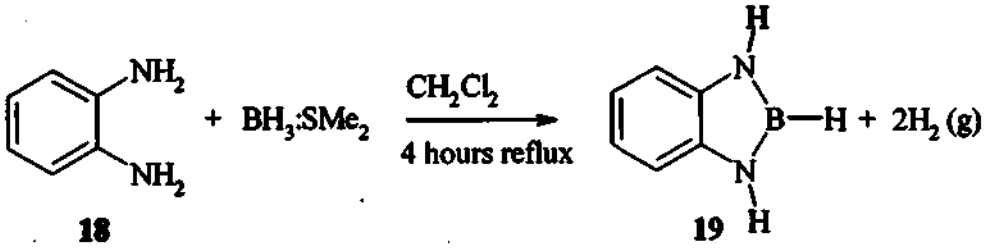
We subsequently focussed our attention on the alkylaminoboranes.To date very little research has been conducted on these compounds, and we felt that this was a logical extension to the compounds already investigated. It was expected that the nitrogen containing borolanes would be significantly less reactive than the sulfur or oxygen analogues, consequently it was felt this would make a very interesting class of compounds to investigate. To date no reports in the literature report the hydroboration of an alkene with a alkylaminoborane, adding to the interest in investigating these compounds.

Another factor influencing the move to the study of the alkylaminoboranes was the somewhat smelly nature of the thiols. During studies conducted using thiols, very smelly and offensive fumes that caused nausea and headaches were released. About a drop of sulfur compound was capable of contaminating the whole laboratory, and it became an excuse for a couple of research students not to come to the laboratory. If the reactions were conducted in the fume cupboard equipped with extractor fans and a scrubber, fumes extracted to the atmosphere were offensive to students and lecturers passing by the chemistry department.

It also appears in the ***Guinness Book of World Records***[121] that thiols (also known as mercaptans) are the smelliest man-made compounds in the world. It has also been reported by Williams *et al.*,[122] (skunk chemistry specialists) that the defence secretion of the skunk contains seven major smelling components. Two of these are thiols, which are responsible for the strong smell. All the above mentioned problems had to be circumvented by switching our attention to the less offensive compounds, which are the nitrogen-based derivatives.

3.4.1 Synthesis of Benzo-1,3,2-diazaborolane

The reaction of 1,2 phenylenediamine (**18**) with BH_3:SMe_2 in a 1:1 mole ratio under reflux, afforded a light yellow liquid of benzo-1,3,2-diazaborolane (**19**) (Scheme 58) in an excellent yield of 95%. The ^{11}B NMR analysis of this compound showed a clean spectrum with only one doublet at 23.9 ppm (Figure 3.15**A**).



18 **19**

Scheme 58

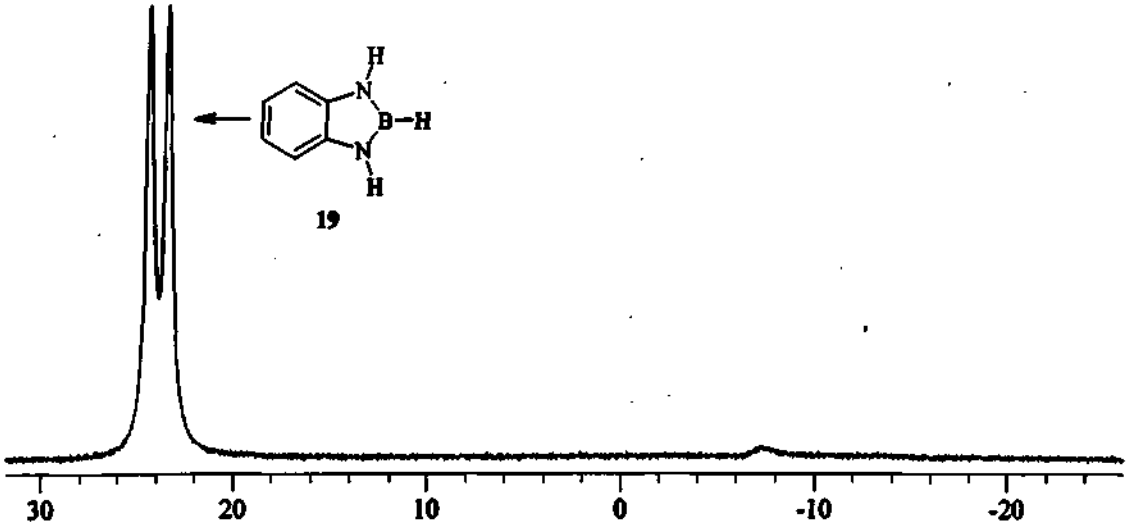


Figure 3.15A ^{11}B NMR spectrum of **19** obtained after 4 hours of reflux in CH_2Cl_2

The formation of benzo-1,3,2-diazaborolane (**19**) was confirmed by the MS analysis (Figure 3.15B). The MS analysis showed an intense base peak with a molecular ion of 118.13 *m/z* ratio and a relative abundance of 100%. This was then assigned to benzo-1,3,2-dithiaborolane (**19**) (Mw = 117.9 g/mol).

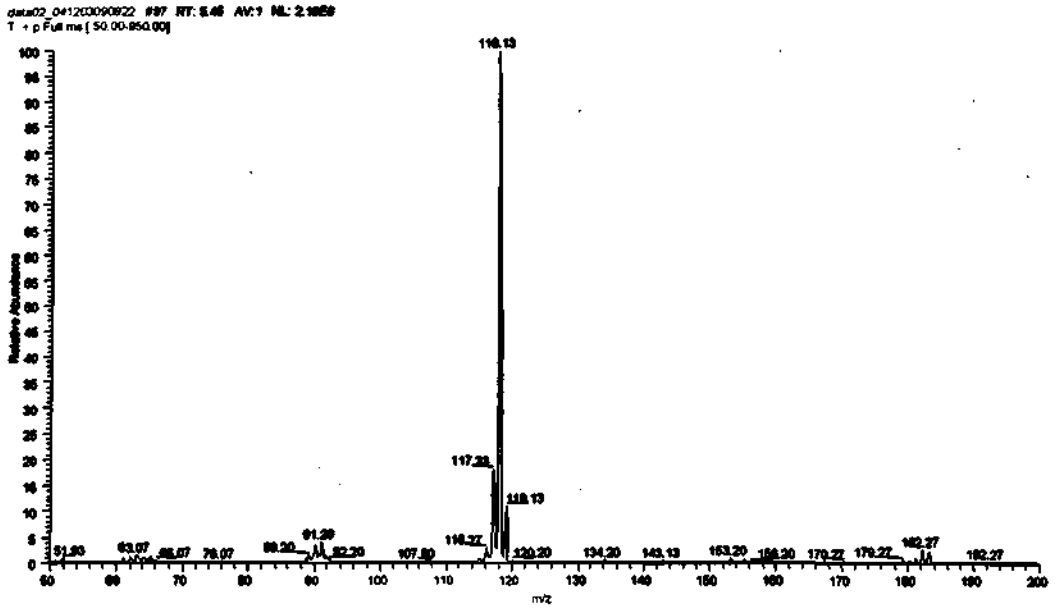
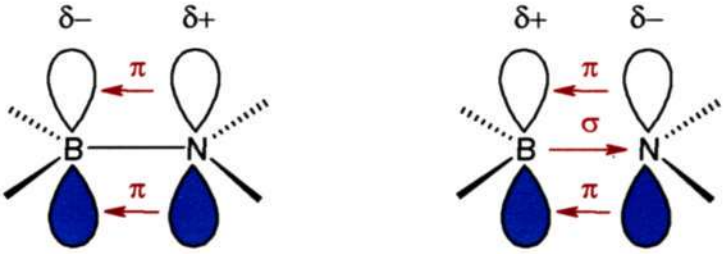


Figure 3.15B MS trace of benzo-1,3,2-diazaborolane (**19**)

Benzo-1,3,2-diazaborolane is substantially less sensitive to air and moisture than its oxygen and sulfur analogues (benzo-1,3,2-dioxaborolane and benzo-1,3,2-dithiaborolane). This property makes this reagent easier to handle. In addition, no disproportionation, dimerization or polymerization was observed; even when the reaction mixture was heated for a week at 110 °C. This observation is significant as it indicates that the lone pair electrons from the nitrogen substituent interact with the empty p-orbital of the boron atom, thus stabilising the compound from nucleophilic attack by the $^{-}$OH from the moisture.

These observations are supported by the study of back-donation and dipole moments of B-X bond conducted by Denk *et al.*[123] The mesomeric presentation of the π-back-donation obtained in this study showed a shifting of π-electrons and also suggested a strong negative partial charge on boron, and a strong positive partial charge on the nitrogen atom (Scheme 59 A). However, experimental determination of dipole moments showed that there is a very small negative partial charge on boron and a very small positive partial charge on the nitrogen atom.

It was found that the boron atom is actually the positive end of the dipole and that the π-electron rearrangement is over compensated by the polarization of the σ–bond between boron and nitrogen. Since nitrogen is more electronegative, the resultant net charge of electron density makes nitrogen the negative end of the dipole. It was also found that there is a flow of π–electrons from the nitrogen orbitals to the vacant p-orbital on the boron through intramolecular back-donation. An σ- effect was also observed - the boron atom donates σ–electrons to the nitrogen atom (Scheme 59 **B**).[123]



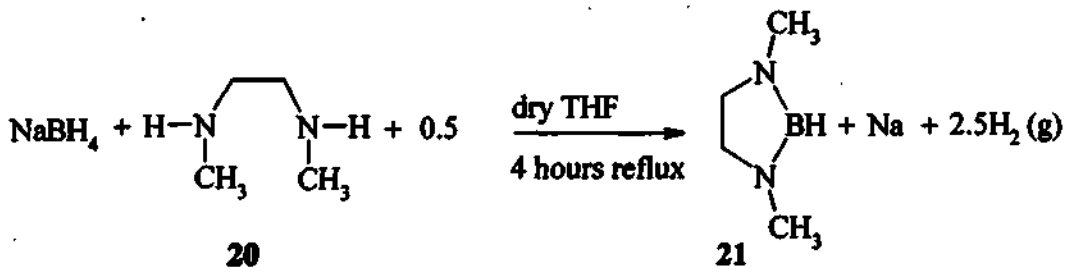
Scheme 59 **A** shows a charge distribution for a mesomeric structure (π only), and **B** shows a true charge distribution (σ and π)

This high degree of stability developed in this compound makes it less susceptible to nucleophilic attack by ^{-}OH. The reduced Lewis acidity of the B-H group impedes this compound from forming dimers.

3.4.2 Synthesis of 1,3-Dimethyl-1,3,2-diazaborolane

1,3-dimethyl-1,3,2-diazaborolane (**21**) was synthesized using $NaBH_4$ as the source of borane instead of BH_3:SMe_2 as proposed by Niedenzu *et al.*[71] *N,N'*-dimethylethane-1,2-diamine (**20**) (Scheme 60) reacted with $NaBH_4$ in a 1:1 stoichiometric ratio in refluxing THF in the presence of iodine solution, which was added slowly prior to refluxing. The role of iodine in the reaction is to capture the sodium ions from $NaBH_4$ to generate the NaI precipitate, this leads to a rapid evolution of hydrogen gas and the formation of BH_3:THF which reacts with *N,N'*-dimethylethane-1,2-diamine on heating. Niedenzu *et*

al.[71] proposed that the reaction goes to completion within 4 hours. However, in our study, the resulting cloudy mixture obtained after 4 hours was filtered and subsequent ^{11}B NMR spectroscopy of the sample indicated (Figure 3.16) a mixture of products and not the target molecule as expected. Only *ca.* 58% of the target molecule was present as indicated by the doublet at 29.2 ppm for B-H coupling. 5% of a mono substituted borane, shown as a minor triplet at 0 ppm was also formed[¶], a quartet at -15.3 ppm was attributed to BH_3:*N,N'*-dimethylethane-1,2-diamine complex *ca.* 32% yield, and lastly a quintet at -42.1 ppm for unreacted $NaBH_4$ *ca.* 2% yield.



Scheme 60

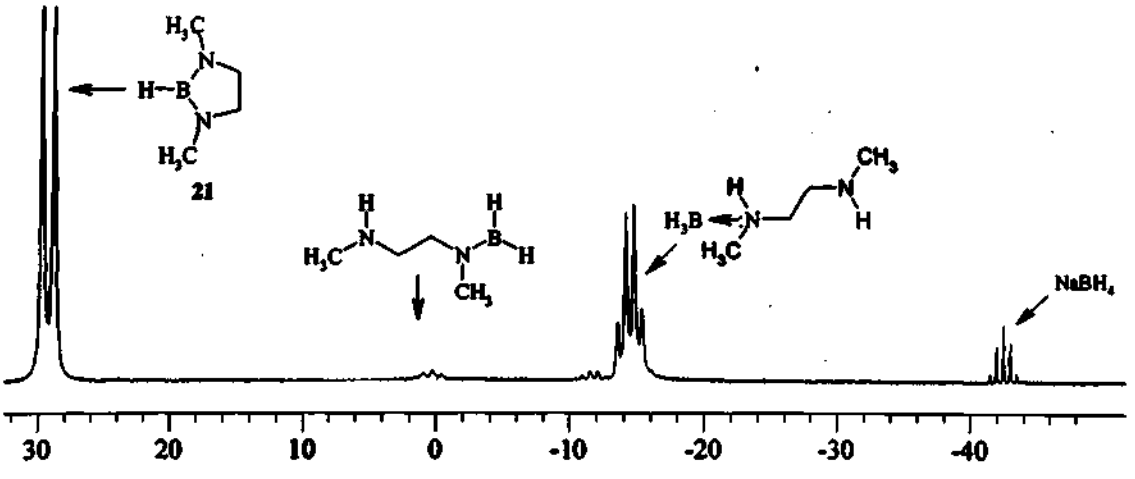


Figure 3.16 ^{11}B NMR spectrum obtained after 4 hours refluxing, showing the product distribution obtained from the reaction of (20) with $NaBH_4$ in boiling THF

[¶] Confirmed with a *J*-resolved NMR spectrum.

The impeded rate of formation of 1,3-dimethyl-1,3,2-diazaborolane (21) was attributed to the increased steric hindrance due to the bulky methyl substituents on the two nitrogen groups; this would hinder the interaction of the nitrogen with the boron centre. The reflux was allowed to proceed for a further 10 hours in order to drive the reaction to completion. After this period had elapsed, a clear liquid with a precipitate of NaI was obtained after cooling the reaction mixture. ^{11}B NMR analysis (Figure 3.17A) of the liquid portion showed a doublet at 29.2 ppm attributed to the product 1,3-dimethyl-1,3,2-diazaborolane (21) in 80% yield. A new singlet was observed at 23.9 ppm and this was assigned to *N,N'*-Bis-(1,3-dimethyl-[1,3,2]diazaborolidin-2-yl)-*N,N'*-dimethyl-ethane-1,2-diamine, the disproportionation product (*ca.* 4%).

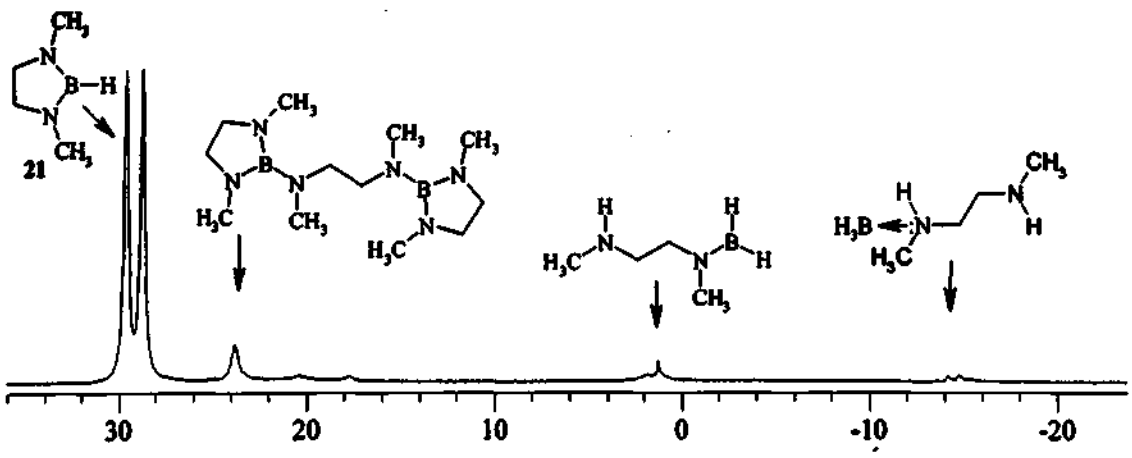


Figure 3.17A ^{11}B NMR spectrum showing about 80% of 1,3-dimethyl-1,3,2-diazaborolane (21) achieved after boiling for 14 hours in THF

3.5 Computational Rationalization of the Disproportionation of Oxygen-, Sulfur-, and Nitrogen-Based Borolanes

1,3,2-Dioxaborolane, 1,3,2-dithiaborolane, and 1,3,2-diazaborolane (from the left in Figure 3.17B) were used in the modelling study, in order to rationalise the Disproportionation level observed experimentally for each compound. DFT with B3LYP

method and LACV3P+** basis set level of theory was employed. Geometry optimized borolanes are presented in figure 3.17**B**.

Figure 3.17B Showing geometry optimized structures of O-, S-, and N-based borolanes.

Table 3.2 indicates the B-H and B-X[Θ] bond lengths computed for geometry optimized molecules at this level of theory. The B-X bond length measurements showed the bond length increased in following trend: B-O < B-N < B-S. This trend did not account for the observed disproportionation. Looking at the electrostatic charges on the boron atom for each compound, for the oxygen derivative, it was found that the boron atom in the oxygen derivative possessed a highest percentage of positive character, followed by the nitrogen derivative then the sulfur derivative. The percentage of electronegative character on the hydrogen atom of each compound also showed the same trend: -O-B-H > -N-B-H > -S-B-H. All these values did not support the disproportionation trend observed experimentally.

Further computational studies on the availability of the p_z- symmetry orbital on the boron atom, showed that the oxygen-based borolane has the orbital on boron with the p_z symmetry (Figure 3.17**C**) on the LUMO+1. Whereas for the sulfur derivative, this orbital was not found in the LUMO, LUMO+1, and LUMO+2 that were computed. The nitrogen derivative displayed the p_z orbital in the LUMO+2.

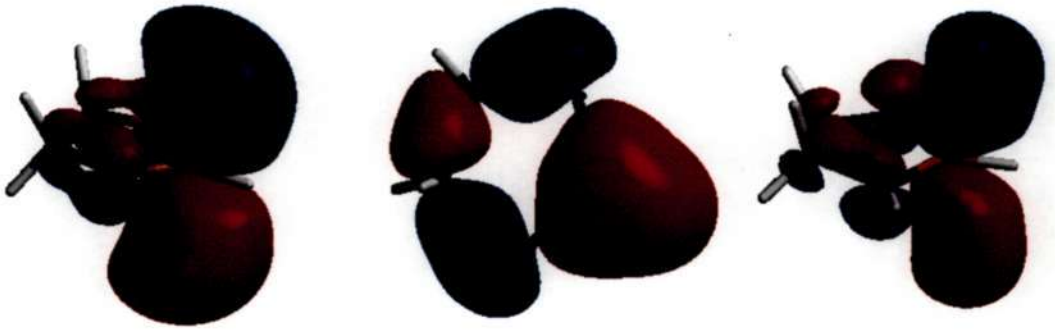
[Θ] X represents the heteroatom, that is oxygen, sulfur, and nitrogen atoms.

The model was also set to compute the availability of the HOMO orbitals on each heteroatom. The oxygen derivative showed a HOMO in both oxygens with a p_z symmetry. the sulfur borolane showed a HOMO-4 with p_z symmetry on one sulfur atom, and the nitrogen derivative showed a HOMO with p_z symmetry on both atoms. The energies of these orbitals are given in Table **3.2**.

Table 3.2 Parameters obtained from the modelling study

		1,3,2-dioxaborolane	1,3,2-dithiaborolane	1,3,2-diazaborolane
Dihedral Angle		0°	40.8°	23.0°
Charges	H	-0.169	-0.021	-0.097
	B	0.696	0.164	0.283
	X	-0.516	-0.217	-0.559
Bond length (Angstrom)	B-H	1.182	1.183	1.187
	B-X	1.366	1.794	1.419
LUMO (au)	+1	0.00649	-0.01321	
	+2		0.00405	0.02346
	+3		0.01720	
HOMO (au)		-0.29207	-0.24363	-0.22391
Energy gap (au)		(LUMO+1 – HOMO) = 0.29207	(LUMO+3 – HOMO) = 0.26083	(LUMO+1 – HOMO) = 0.24737

The HOMO-LUMO gap energies obtained showed that the gap in the oxygen derivative (0.29207 au) is larger than that for the sulfur derivative (0.26083 au) and much larger than that for the nitrogen derivative. This interesting observation revealed that the HOMO and the LUMO orbitals with the p_z symmetry are far apart for 1,3,2-dioxaborolane, thus reducing the amount of π-back bonding, leading to an unstable compound that is more likely to disproportionate. Whereas for 1,3,2-dithiaborolane, the energy gap is slightly lower resulting in a reduced level of disproportionation. For 1,3,2-diazaborolane the gap is smaller, which allows for more pronounced π-back bonding.



1,3,2-dioxaboralane 1,3,2-dithiaborolane 1,3,2-diazaborolane

Figure 3.17C Showing the availability of the vacant p_z-orbital of the boron atom of each geometry optimized structure.

3.6 Hydroboration Studies

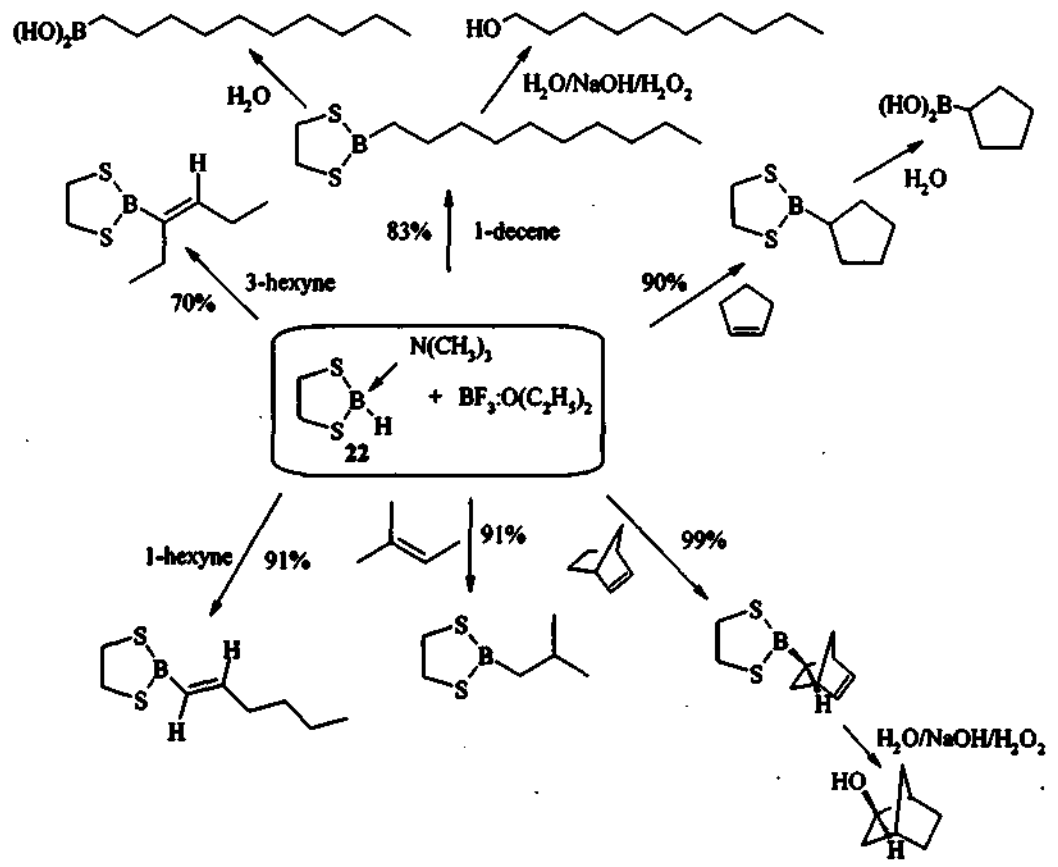
3.6.1 Introduction

The focus of this study was to explore the reactivity and chemistry of the novel heteroatom containing alkylthio- and alkylaminoboranes that we have developed synthetic routes for.

The studies were designed to expose the trends in the reactivity of these compounds, as well as to explore the key issues such as isomerisation and displacement which are of commercial importance in this study. Our focus was limited to those reagents with only a single site available for hydroboration in order to prevent possible addition reactions, monomer dimer equilibria, and redistribution equilibria as illustrated in Section 3.1.

3.6.2 Hydroboration of 1-Octene with 1,3,2-Dithiaborolane

Thaisrivongs *et al.*[53] have reported that 1,3,2-dithiaborolane can be obtained as a stable complex when treated with trimethylamine. Thaisrivongs *et al.*[53] also reported that treatment of 1,3,2-dithiaborolane trimethylamine complex (22) (Scheme 61) with diethyl-trichloroborane or trifluoroborane resulted in an efficient hydroboration of a representative group of alkenes and alkynes into alkyl- and alkenyl-1,3,2-dithiaborolanes at 50 °C in benzene (Scheme 61).[53]



Scheme 61

Our studies were all conducted in quartz NMR tubes sealed with rubber septa parafilm "M"®. The olefin was injected into the NMR tube with 1,3,2-dithiaborolane dimethyl sulfide complex (7) in the presence of the disproportionation product (8). It was observed that 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8) was not involved in any

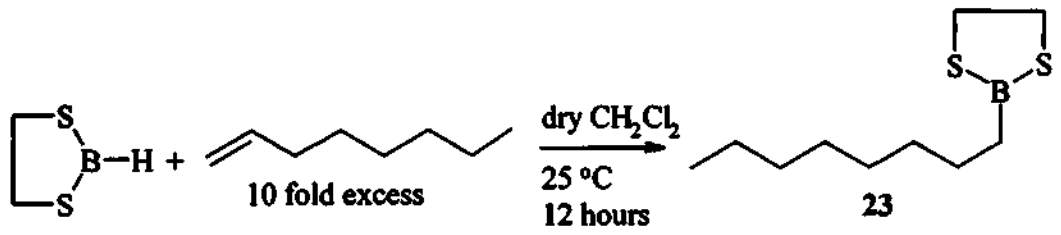
hydroboration reactions, as it does not possess any free sites for it to react with the alkene. It was also interesting to note that no further disproportionation of 1,3,2-dithiaborolane was observed during the hydroboration process. The formation of octyl-1,3,2-dithiaborolane was shown by a broad singlet resonating at 70.4 ppm (Figure 3.18) and this was the desired product of the reaction. No other products were formed in this reaction, no intermediates were observed spectroscopically. At this point it was decided to explore the use of ^{11}B NMR spectroscopy in order to obtain kinetic information about our reactions, which would be important to rationalise our observations.

The use of ^{11}B NMR spectroscopy to identify and monitor the formation of the hydroborating agent synthesised in the research was found to be an accurate technique. As a result, it was employed to monitor the progress of the hydroboration reaction and also indicated that it offers better insight into the process as opposed to GC, in which samples are taken during the process and quenched with alkaline hydrogen peroxide and monitor the alcohol formation. The samples taken for GC are no longer useful and the formed alkyboronate ester structure cannot be further analysed. Samples eluted off the column are also not recyclable for structural analysis.

It was of great importance to conduct concentration and temperature dependence studies because they yield the kinetic and thermodynamic parameters for the hydroboration of olefins with the synthesized compounds.

3.6.2.1 Concentration Dependence Study

The following reactions were conducted under pseudo-first order conditions, this was done in order to obtain the observed rate constants (k_{obs}) and the second order rate constant (k_2) for the hydroboration of 1-octene with 1,3,2-dithiaborolane dimethyl sulfide complex (Scheme 62).



Scheme 62

In this study the concentration of 1,3,2-dithiaborolane was kept constant while that of 1-octene was varied from 10× to 25×. It was impossible to monitor beyond 25× because the reactions were too fast and went to completion within a first few hundred seconds after mixing the reagents.

^{11}B NMR spectroscopy was then used to monitor the progress of the hydroboration reaction (Figures 18.3 and 19.3). Array **A** shows the disappearance of the reactant (1,3,2-dithiaborolane) as time increases while array **B** shows the progress of the formation of the desired alkylboronate.

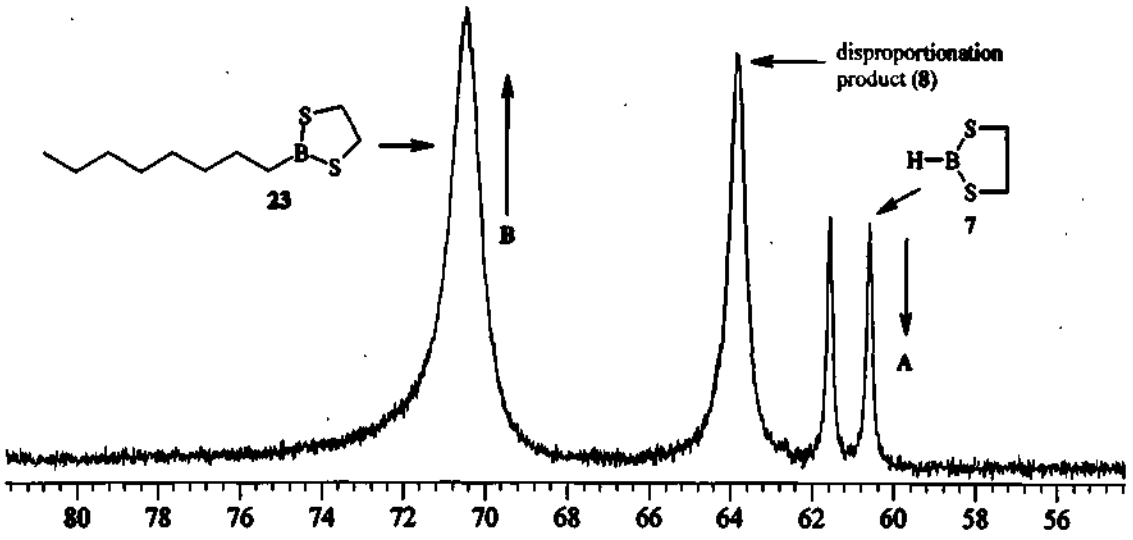
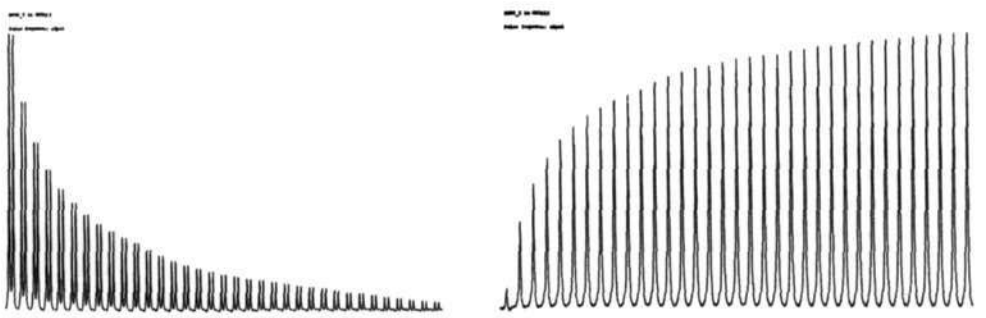


Figure 3.18 ^{11}B NMR spectrum showing the progress of a typical hydroboration of 1-octene with 1,3,2-dithiaborolane



Array **A** Array **B**

Figure 3.19 Shows the arrayed reagent depletion (array A) and product formation (array B)

The integrals of the reactant and product were converted into concentrations and plotted against time in order to obtain the observed rate constants and the second order rate constants.

Using the Microcal™ Origin™ 5.0 software and fitting the first-order exponential decay curves to the NMR data, the following plots were observed where the experimental data is shown as squares and smooth curve is the first order exponential decay. Taking the inverse of t1 obtained from the software's exponential decay curve fitted in these plots gives the observed rate constant (k_{obs}) at each concentration.

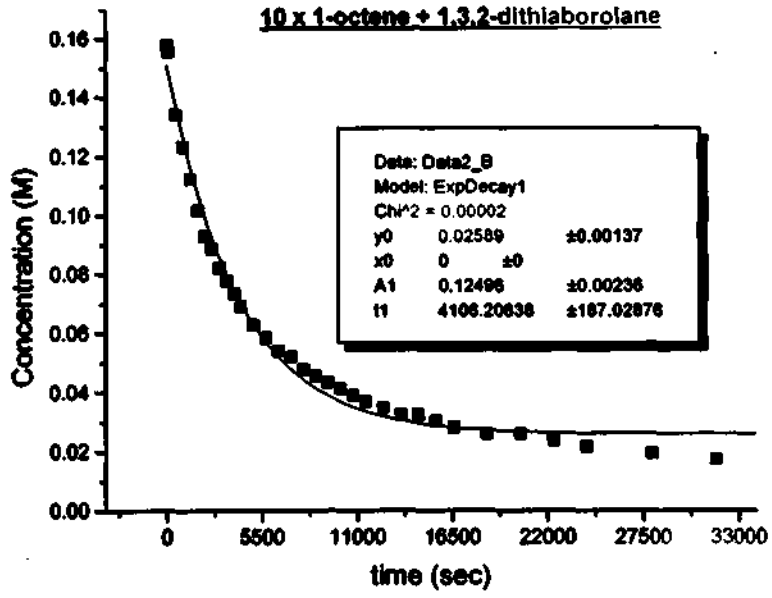


Figure 3.20

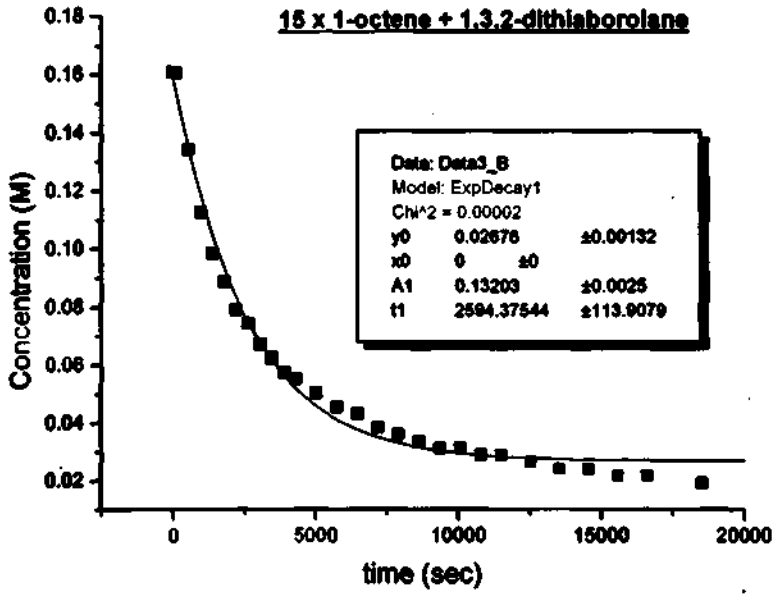


Figure 3.21

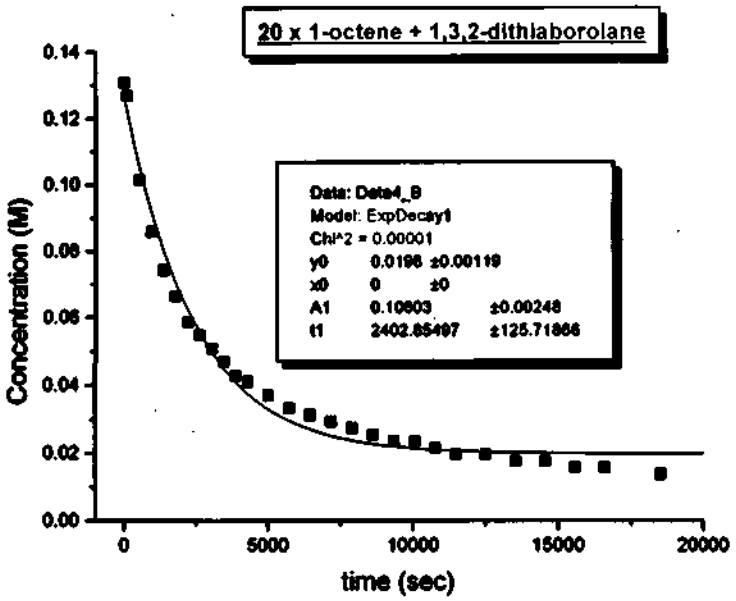


Figure 3.22

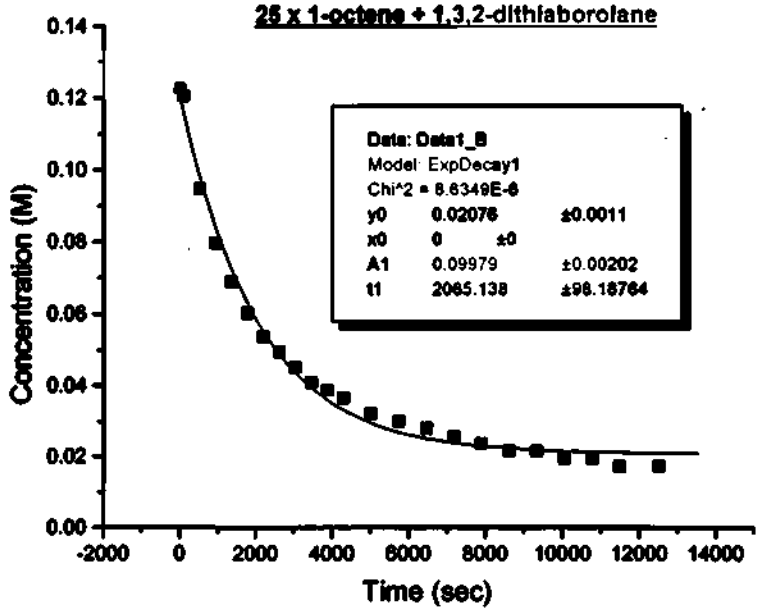


Figure 3.23

From the above plots, the observed rate constants were obtained for each concentration. In order to obtain the second order rate constants, the observed rate constants were plotted against concentration and the plot shown in Figure 3.24 was obtained. The slope of this graph is the second order rate constant $k_2 = (1.548 \pm 0.009) \times 10^{-4}\ M^{-1}s^{-1}$.

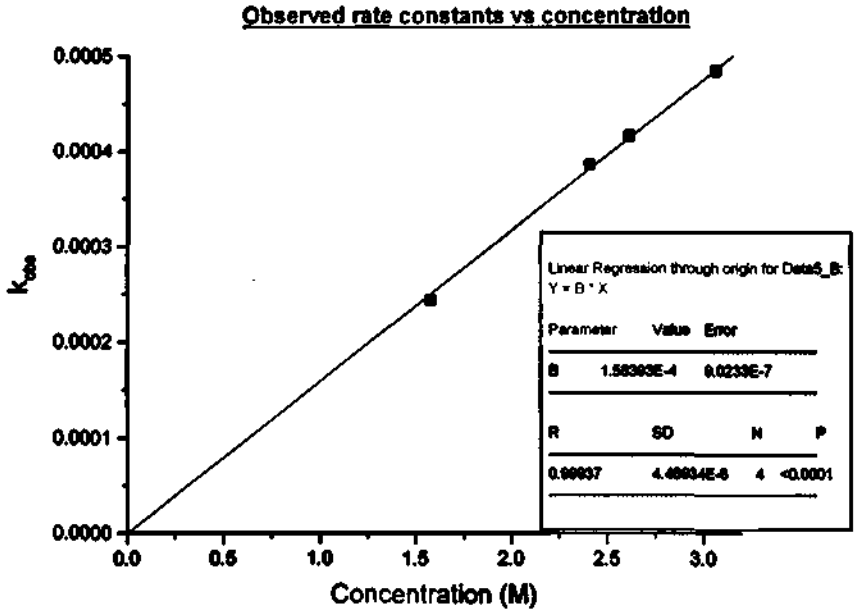


Figure 3.24

3.6.2.2 Temperature Dependence Study

The temperature dependence study involved keeping the concentration of both the hydroborating agent and olefin constant and vary the reaction temperature, in order to get the activation parameters of the hydroboration reaction (that is, the entropy of activation $\Delta S^{\neq}$ and the enthalpy of activation $\Delta H^{\neq}$). The reaction temperature was varied from 20 to 35 °C - it was unfavourable to go beyond 35 °C because our reactions were conducted in CH_2Cl_2 as the reaction solvent which boils at 40 °C. For each temperature, concentration vs. time graphs were plotted and these are shown below (Figures 3.25 to 3.28).

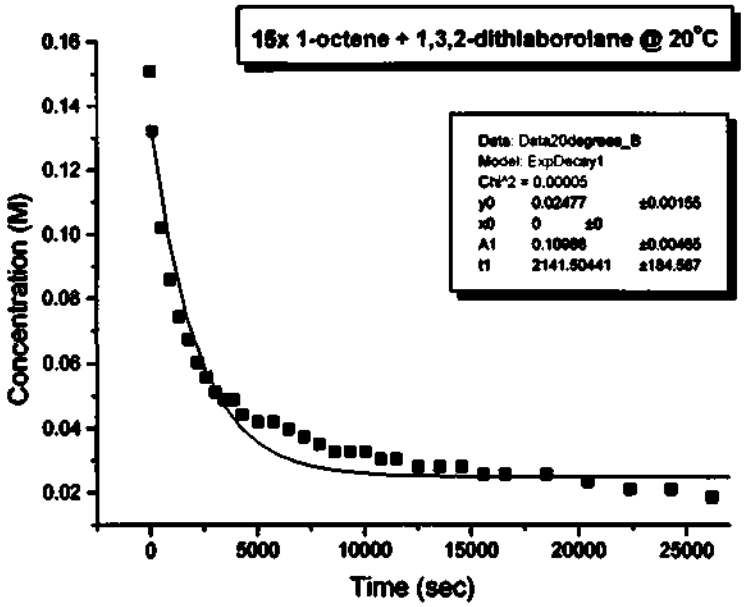


Figure 3.25

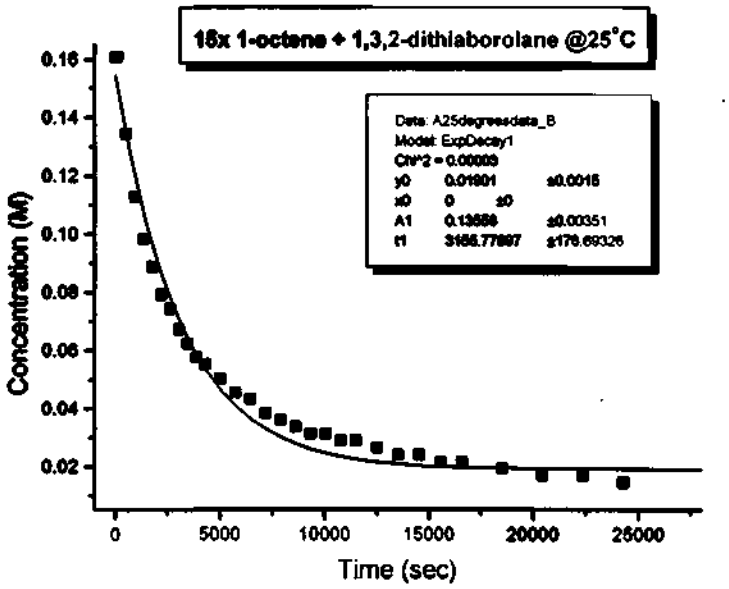


Figure 3.26

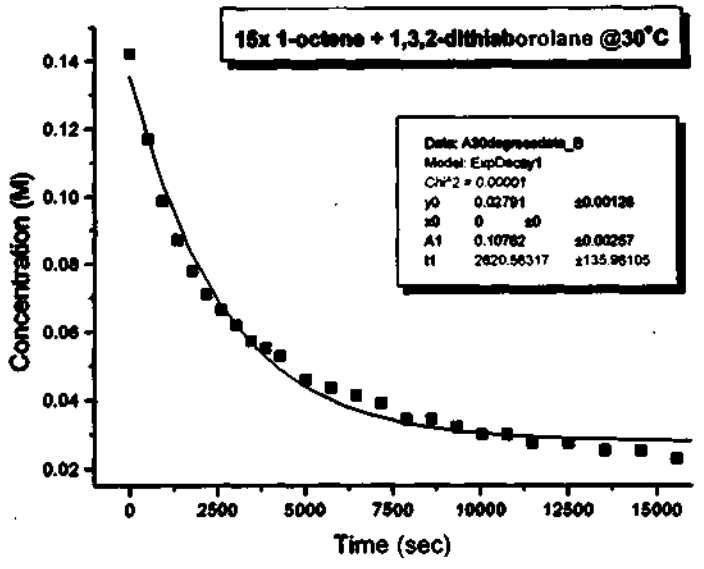


Figure 3.27

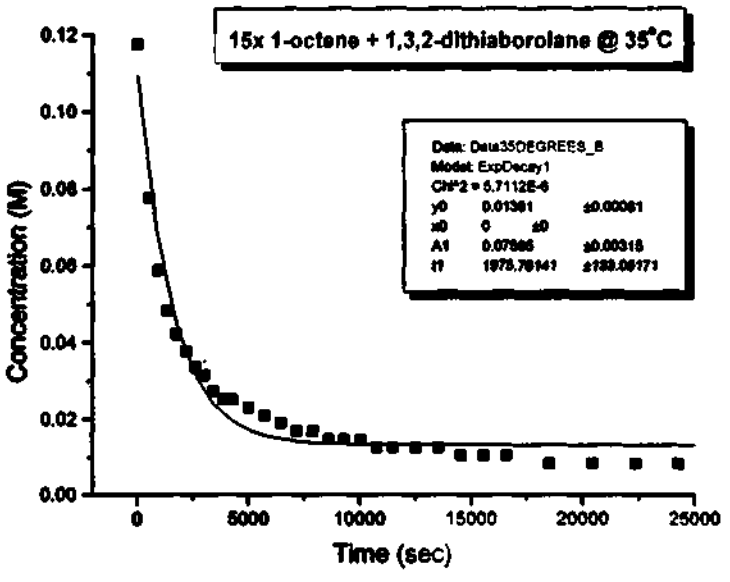


Figure 3.28

The observed rate constants from the above temperature dependence study were used to plot the Eyring plot (Figure 3.29), the slope and the y-intercept of this plot were used to determine the activation parameters using Equation 4.3, where R is the gas constant.

$$\Delta H^{\ddagger} = Slope \times R$$
$$\Delta S^{\ddagger} = (\text{y - intercept} - 23.8) \times R$$

Equation 4.3

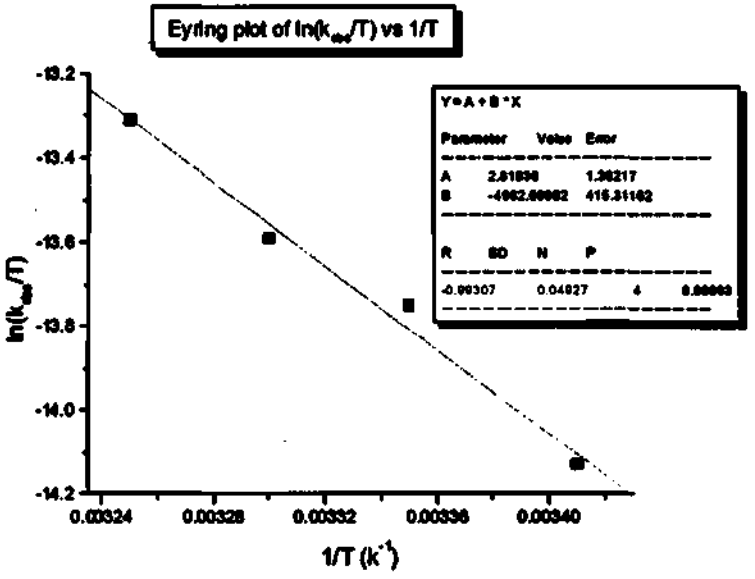
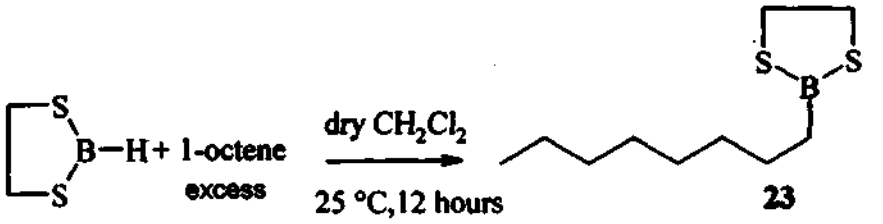


Figure 3.29

From Figure 3.29, the enthalpy of activation ($\Delta H^{\ddagger}$) was found to be (- 41.30 ± 3.45 kJmol^{-1}) which indicated that the hydroboration of 1-octene was an endothermic reaction, the entropy was found to be (-174.45 ± 11.49 JK^{-1} mol^{-1}). This large and negative value indicates that reagents underwent an associative mechanism (i.e., the hydroborating agent and the olefin unite to form a four-centre transition state) prior to formation of the product octyl-1,3,2-dithiaborolane (23) (Scheme 62).



k_2 =(1.548 ± 0.009) x10 $^{-4}$ $M^{-1}s^{-1}$
$\Delta H^{\neq}$ =(-41.30 ± 3.45) $kJmol^{-1}$
$\Delta S^{\neq}$ =(-174.45 ± 11.49) $JK^{-1}mol^{-1}$

Scheme 62

3.6.3 Hydroboration of 1-Octene with 1,3,2-Dithiaborinane

This reagent was readily synthesized and investigated in much the same manner as 1,3,2-dithiaborolane. Whilst it was expected that there would be little difference in the thermodynamic values obtained it was seen as an important exercise to ensure the validity of our experimental technique, though one may expect differences in more sterically demanding non-terminal alkenes. 1,3,2-Dithiaborinane (9) is a six membered ring system while in contrast, 1,3,2-dithiaborolane is a five membered ring system. Concentration and temperature dependence studies were performed on this reagent as in the preceding Section, and the observations are discussed in the following sub-sections.

3.6.3.1 Concentration Dependence Study

The same reaction conditions as that of 1,3,2-dithiaborolane were employed in this study. The concentration of 1-octene was varied from 10× to 25× and that of 1,3,2-dithiaborinane was fixed. The following plots were observed from percentage integrals converted to concentrations.

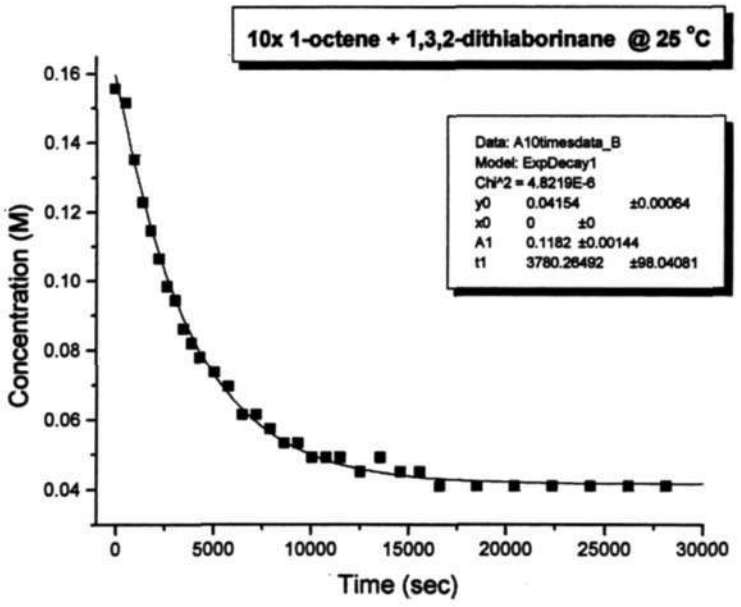


Figure 3.30

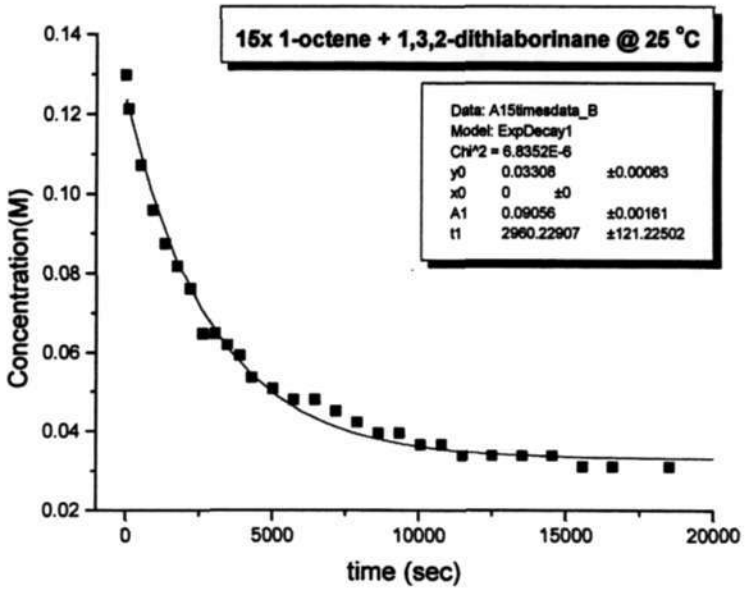


Figure 3.31

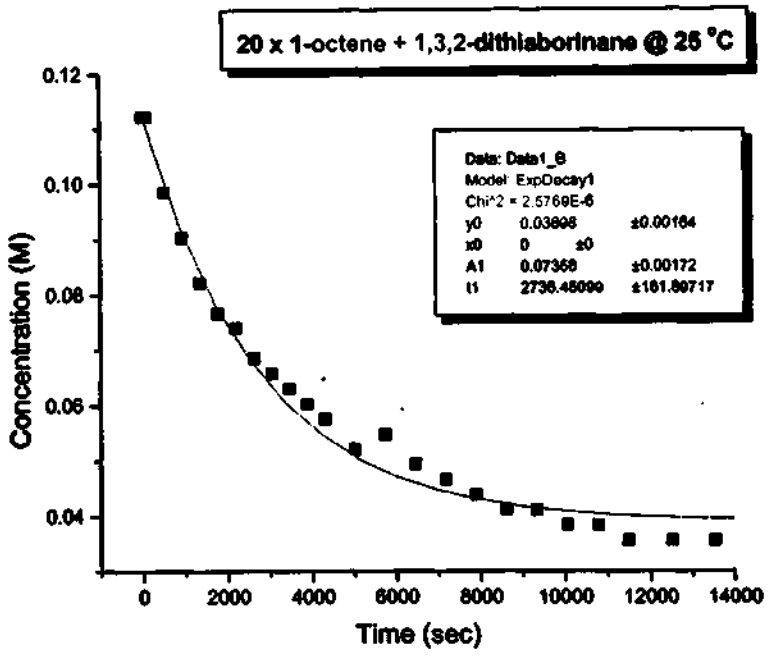


Figure 3.32

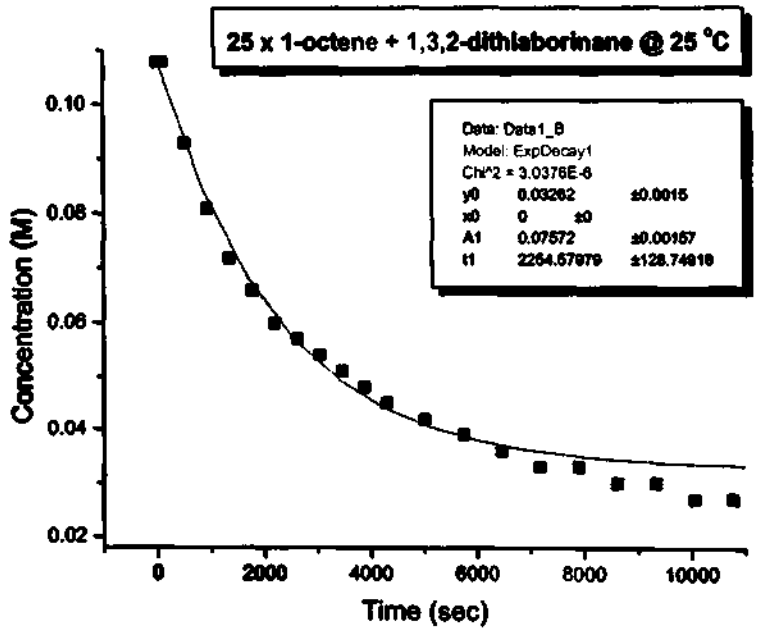


Figure 3.33

The observed rate constants (k_{obs}) at each concentration were plotted against time, and the resulting k_{obs} *vs.* concentration linear plot (Figure 3.34) gave a straight line with a slope correspond to the second order rate constant (k_2), and this was found to be (1.652 ± 0.013 $\times 10^{-4}$ $M^{-1}s^{-1}$)

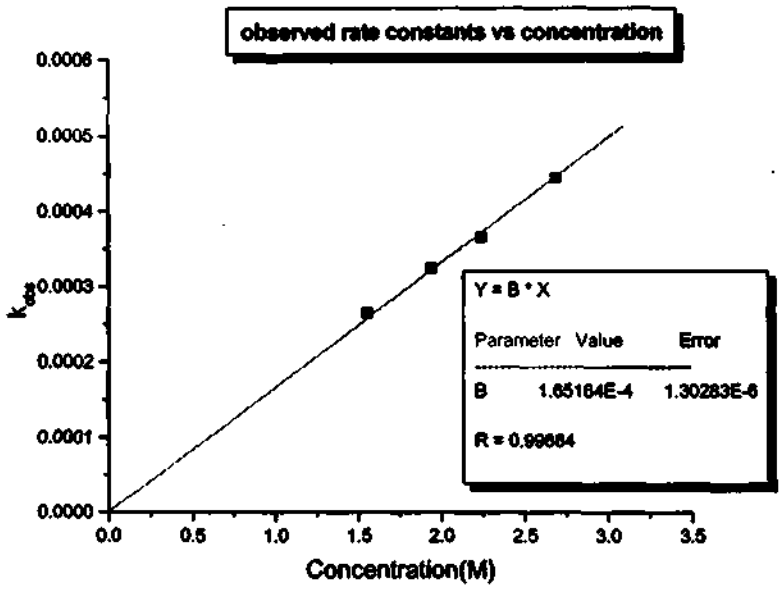
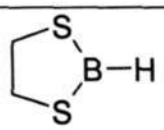
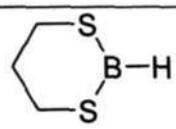


Figure 3.34

The results obtained from concentration dependence studies for both (7) and (9) are summarized in Table 3.3 below.

Table 3.3 Shows the observed rate constant for each concentration

		 *1,3,2-dithiaborolane*	 *1,3,2-dithiaborinane*
Temperature (°C)	Concentration (M)	$k_{obs}/10^{-4}$ (s^{-1})	$k_{obs}/10^{-4}$ (s^{-1})
25	10×	2.436	2.645
25	15×	3.855	3.235
25	20×	4.162	3.650
25	25×	4.842	4.435

When one compares the observed rate constants for both reagents at each concentration and fixed temperature (Table 3.3), it can be seen that both reagents hydroborate 1-octene at almost the same rate, so not surprisingly, the ring size does not seem to have any significant role in hindering or facilitating the reaction at the terminal position. This was also shown by the fact that second order rate constants for both reactions are of the same order of magnitude. Temperature dependence studies were also explored in order to obtain the activation parameters for 1,3,2-dithiaborinane and to see if these values support the conclusions drawn from concentration dependence study.

3.6.3.2 Temperature Dependence Study

In this study, the rate constants were determined for a range of temperatures keeping the concentrations of 1,3,2-dithiaborinane and 1-octene constant, while the temperature was varied from 20 to 35 °C in steps of 5 °C as in Section 3.4.1.2 (refer to Figures 3.35 to 3.38)

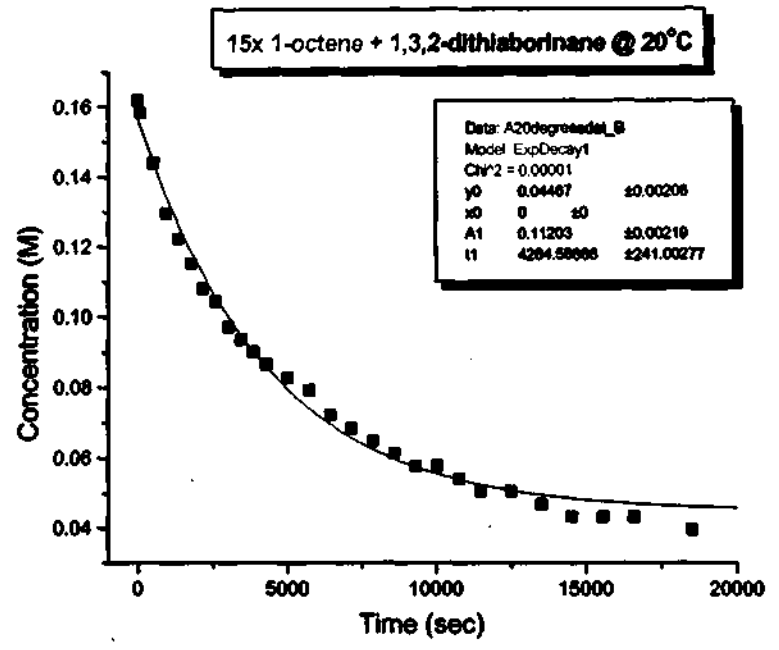


Figure 3.35

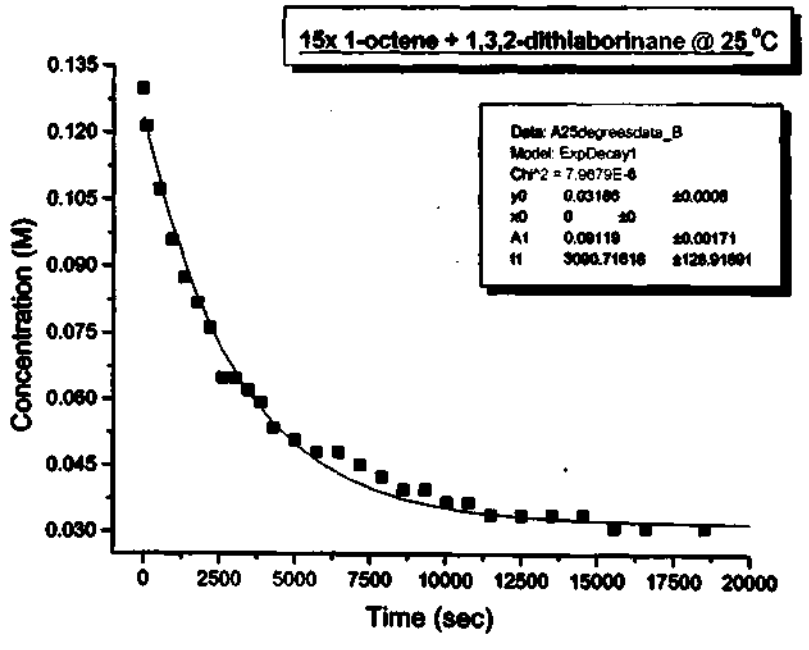


Figure 3.36

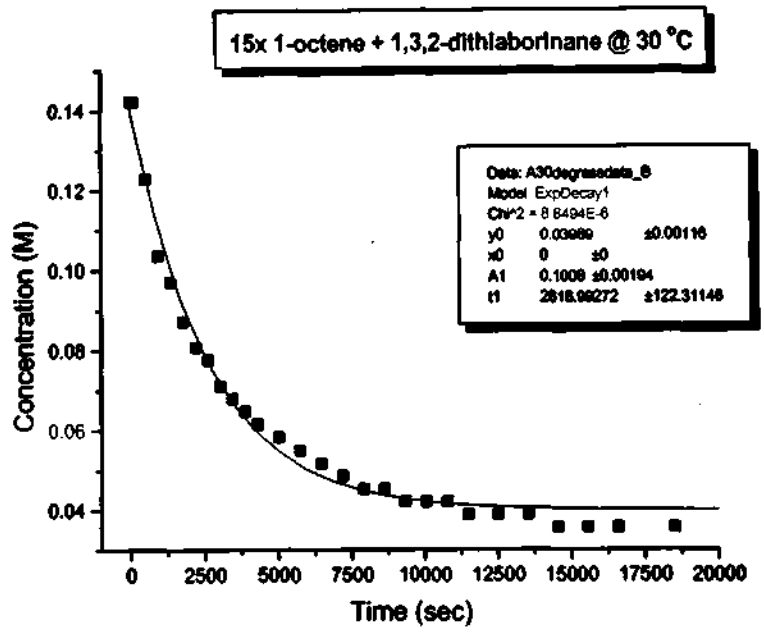


Figure 3.37

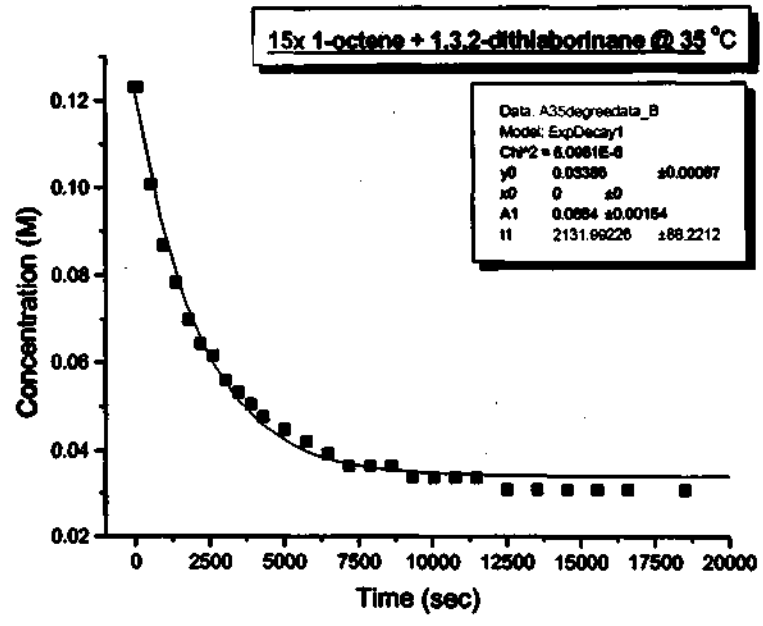


Figure 3.38

The slope and the y-intercept obtained from the plot of $\ln(k_{obs}/T)$ vs. 1/T (also known as the Eyring plot) (Figure 3.39) were fitted to Equation 3.4. From this Equation $\Delta S^{\neq}$ and

$\Delta H^{\neq}$ were calculated. $\Delta S^{\neq}$ was found to be (-208.49 ± 11.52 $JK^{-1}mol^{-1}$) and $\Delta H^{\neq}$ was found to be (-31.02 ± 3.46 $kJmol^{-1}$).

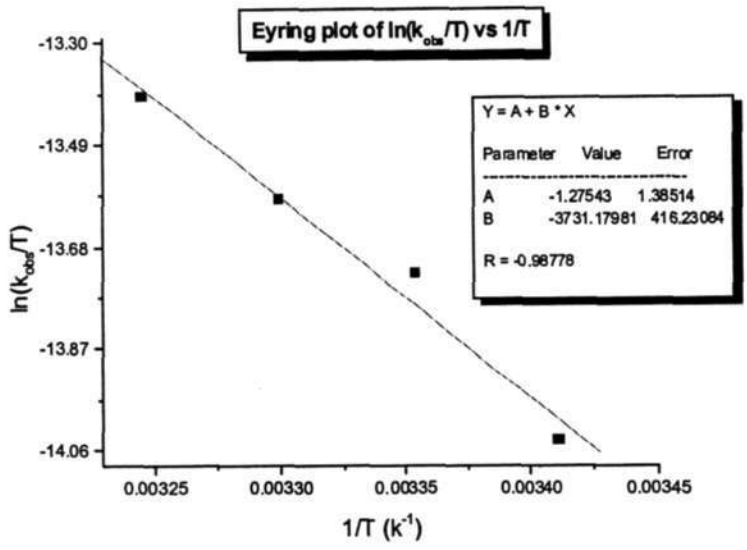
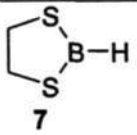
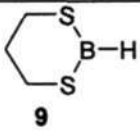


Figure 3.39

The calculated values for second order rate constants (k_2), entropies and enthalpies obtained for the hydroboration of 1-octene using 1,3,2-dithiaborolane and 1,3,2-dithiaborinane (sections 3.4.1 to 3.4.2) are shown in Table 3.4.

Table 3.4 The calculated values of the second order rate constant, enthalpy and entropy for both heterocyclic hydroborating agents.

	 **7** *1,3,2-dithiaborolane*	 **9** *1,3,2-dithiaborinane*
K_2 ($M^{-1}s^{-1}$) ×10^{-4}	1.548 ± 0.009	1.652 ± 0.013
$\Delta H^{\neq}$($kJmol^{-1}$)	-41.30 ± 3.45	-31.02 ± 3.46
$\Delta S^{\neq}$($JK^{-1}mol^{-1}$)	-174.45 ± 11.49	-208.49 ± 11.52

At this point, our initial aim was to use the data from the sulfur-based boranes in order to contrast with the nitrogen and oxygen analogues and to compare kinetic and thermodynamic data obtained.**

Table 3.4 summarises the findings and as indicated the $\Delta H^{\neq}$ values for both reagents are small and negative which is indicative of an exothermic reaction. The data is second order for both compounds which implies that the reaction involves two species in the rate determining step of the hydroboration reaction. The $\Delta S^{\neq}$ values obtained for both reagents supported the proposed hydroboration mechanism[22] (Figure 1.3).+ The obtained $\Delta S^{\neq}$ values are large and negative which supports an associative mechanism, whereby the electrons from the π-orbital of the olefinic double bond are donated to the empty p_z-orbital the boron atom. The B-H bond also back donates to the π^*-orbital of the alkene resulting in a concerted 4-center addition.[22]

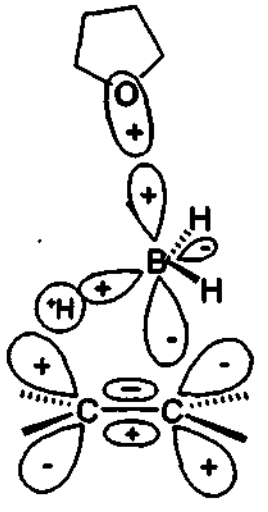


Figure 1.3

** Kinetic studies of 1,3,2-dithiaborolane and 1,3,2-dithiaborinane were conducted prior to the synthesis of the oxygen- and nitrogen- based boranes, hence we were unaware of the disproportionation and stability problems associated with these species.

+ Refer to chapter 1, section 1.3.3, page 11.

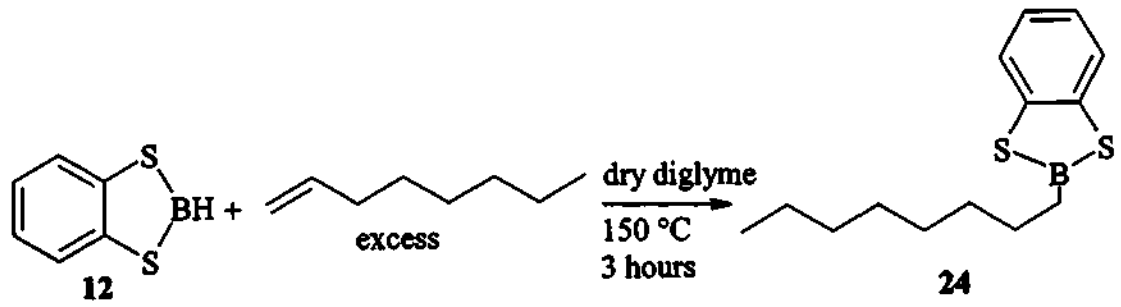
The mechanism shows that the Lewis base involved in the complex also plays a role during the hydroboration process. However, for the purpose of this study it was not deemed significant since the study was merely focused on comparing the role of the heteroatoms contained within the borolane. Due to the difficulties experienced with synthesis of the oxygen analogue of the borolane and synthesis of other sulfur- based boranes, it was unfortunately not possible to conduct a comparative study between the roles of these heteroatoms.[Ψ]

The kinetic and thermodynamic parameters for the hydroboration of 1-octene with 1,3,2,-dithiaborolane (7) and 1,3,2-dithiaborinane (9) given in Table 3.4, were compared to that obtained for $HBBr_2{:}SMe_2$ complex [$k_2 = (34.7 \pm 0.04)\times10^{-4}\ M^{-1}s^{-1}$; $\Delta S^{\neq} = -18 \pm 4\ JK^{-1}mol^{-1}$; $\Delta H^{\neq} = 82.4 \pm 4\ kJmol^{-1}$].[117] The comparison revealed that the hydroboration of 1-octene with 1,3,2-dithiabrolane (7) was 22-fold slower than that with $HBBr_2{:}SMe_2$ complex. Hydroboration with 1,3,2-dithiaborinane (9) was 21 fold slower than that with $HBBr_2{:}SMe_2$ complex. The reduced reactivity observed with the sulfur compounds was attributed to π-back bonding between the boron and the sulfur atoms which hinders the nucleophilic attach by the electrons from the alkene, while on the other hand the Br atoms withdraw electrons inductively from the boron atom thus making it more electrophilic and allows for nucleophilic attack by the alkene.

3.6.4 Hydroboration of 1-Octene with Benzo-1,3,2-dithiaborinane

In order to evaluate the effect of an aromatic system on the reactivity of these compounds, benzo-1,3,2-dithiaborinane (12), which is structurally analogous to 1,3,2-dithiaborolane (7), was synthesised.

[Ψ] Possible studies into the kinetics between the sulfur compounds (i.e. 1,3,2-dithiaborolane and 1,3,2-dithiaborinane) and different types of alkenes could form the basis of another study as very little data exists in the literature and such data would be of scientific interest.



Scheme 63

Benzo-1,3,2-dithiaborinane (12) was freshly synthesized (see Section 3.1.5) and allowed to react with an excess amount of 1-octene in CH_2Cl_2 as the reaction solvent. No reaction was observed spectroscopically at 25 °C even after extended reaction times. The reaction was allowed to stir for 10 days, ^{11}B NMR analysis showed a neat spectrum with only a doublet at 53.4 ppm characteristic of the starting reagent (12). No reaction was observed in refluxing CH_2Cl_2.

The reduced ability of benzo-1,3,2-dithiaborolane (12) to hydroborate 1-octene was attributed to the fact that the aromatic ring has an electron cloud conjugated around the ring. As a result, the electron density is donated to the sulfur substituents which in turn donate electron density to the boron atom, thus making it less electropositive. The decrease in the electrophillic character of the boron atom results in the reduction of the interaction of the B-H bond with the carbon-carbon double bond of the alkene.

The low boiling solvent, CH_2Cl_2 was removed from the reaction mixture *in vacuo*, dry diglyme was introduced into the mixture in order to allow temperature elevation beyond 40 °C. Interesting results were achieved at 150 °C. The mixture was allowed to reflux for 30 min, and the ^{11}B NMR spectroscopic analysis of the sample (Figure 3.40) showed a singlet at 59.6 ppm attributed to the desired product octyl-benzo-1,3,2-dithiaborolane (*ca.* 19%) (24) (Scheme 63). A second singlet was observed at 49 ppm (*ca.* 8%) this was assigned to the disproportionation product. After 3 hours of reflux at 150 °C, about 65% of octyl-benzo-1,3,2-dithiaborolane (24), 21% of the disproportionation product, and 4% of the starting hydroborating agent benzo-1,3,2-dithiaborolane (12) were observed.

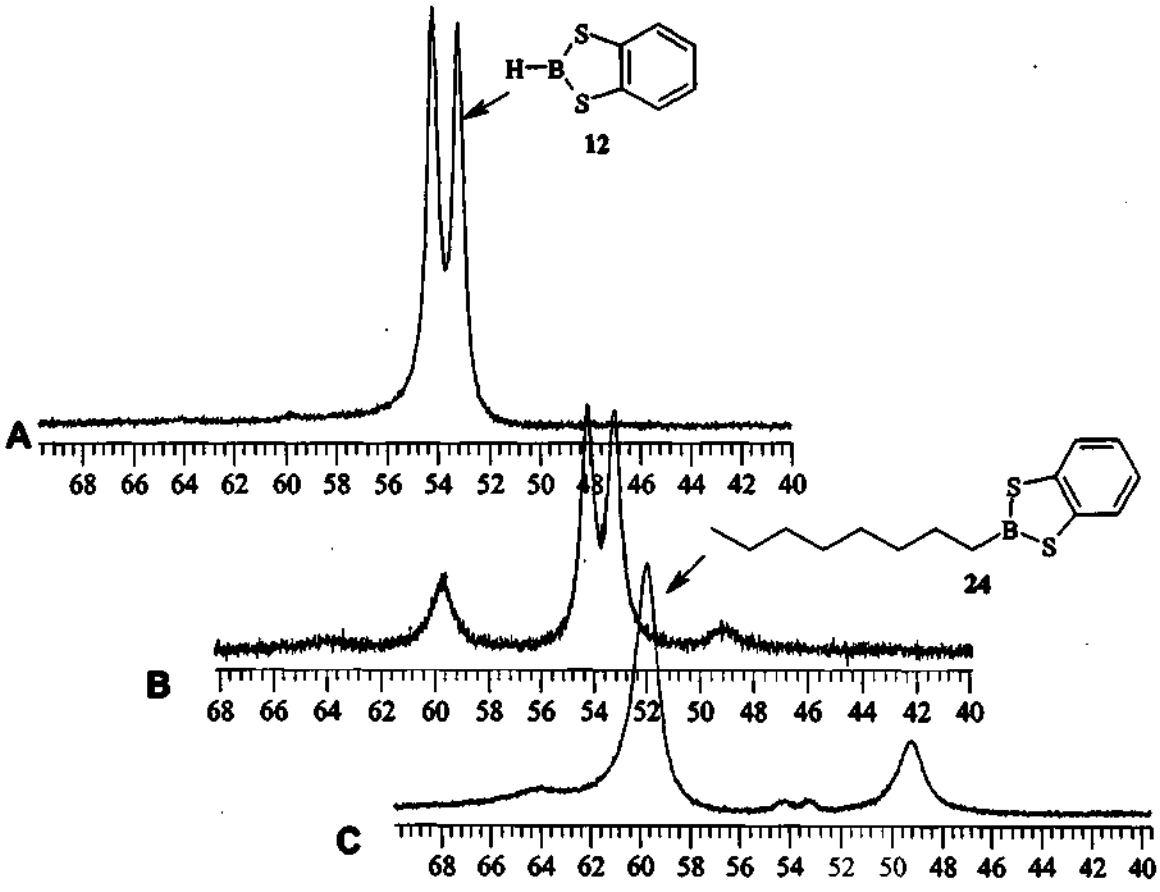


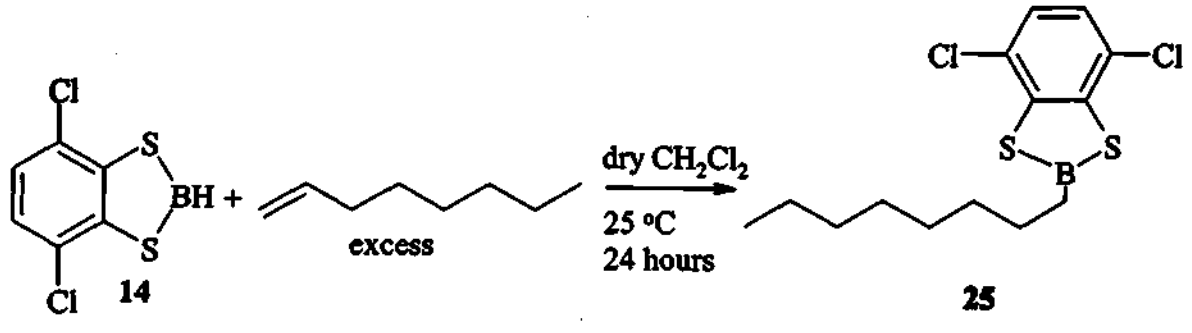
Figure 3.40 ^{11}B NMR spectra obtained from the reaction of benzo-1,3,2-dithiaborolane with 1-octene: **A** shows pure benzo-1,3,2-dithiaborolane, **B** shows the formation of the octylboronate ester after 30 min, and **C** shows a complete depletion of **(12)** to form **(24)**.

Kinetic studies of hydroboration of 1-octene with benzo-1,3,2-dithiaborolane could not be investigated using ^{11}B NMR spectroscopy due to the fact that 150 °C is far beyond the maximum probe temperature for the 500MHz NMR spectrometer used in this research. An alternative approach could involve heating the reaction at elevated temperature and periodically remove aliquots and quenching them with $NaOH/H_2O_2$ solution, however investigations in our group have shown that this method has several flaws in it.[115, 116, 117] Despite this, these results were very interesting and add to the developing picture of the reactivity of these types of species.

3.6.5 Hydroboration of 1-Octene with 4,7-Dichloro-1,3,2-benzodithiaborolane

It has been shown in the above Section that the electrons from the aromatic ring impede the reaction significantly and thus hamper a kinetic study of these reactions. It was decided to explore the general features which control the reactivity of the hydroboration process and then to follow up with a more detailed study at a later date. It was decided to synthesise 4,7-dichloro-1,3,2-benzodithiaborolane (**14**). The objective of attaching the chlorine substituents on the ring was to fine-tune the reactivity of benzo-1,3,2-dithiaborolane (**12**) towards alkenes. It was speculated that Cl groups will withdraw the electron density from the aromatic ring, thus partly removing electron density supplied to the boron atom, and this would make the boron atom more electropositive, thus allowing the B-H bond to interact with the alkene under less demanding conditions.

As the first attempt to test the behaviour of this reagent, it was allowed to interact with excess amount of 1-octene at 25 °C in CH_2Cl_2 for 24 hours (Scheme 64). The ^{11}B NMR analysis of the product mixture displayed only unreacted (**14**) (doublet at 53.2 ppm).



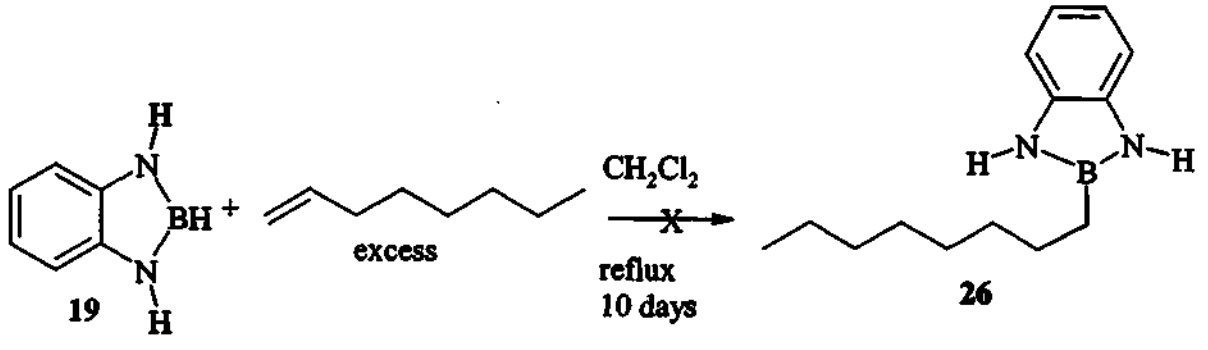
Scheme 64

Disappointingly, no reaction was observed even in refluxing CH_2Cl_2. However, refluxing the mixture in diglyme this resulted in the subsequent hydroboration of 1-octene. From these observations it was noted that the chlorine substituents on the aromatic ring appear to play a minor role in attenuating the reactivity of this compound.

3.6.6 Hydroboration of 1-Octene with Benzo-1,3,2-diazaborolane

As it was discussed in Section 3.3.1 the stability of the diaza derivative was expected, and thus a reduced reactivity compared with its sulfur analogue benzo-1,3,2-dithiaborolane (**12**). Benzo-1,3,2-diazaborolane was freshly prepared (refer to Section 3.3.1) and reacted with 1-octene in CH_2Cl_2 at room temperature under inert atmosphere. No product formation was observed spectroscopically after 24 hours.

The reaction temperature was elevated slowly from room temperature to 40 °C - no reaction was observed after 2 days at this temperature. The reaction mixture was then heated at 100 °C for 10 days - subsequent ^{11}B NMR analysis of this mixture showed a doublet for the hydroborating reagent benzo-1,3,2-diazaborolane (**19**), and no octyl-benzo-1,3,2-diazaborolane (**26**) (Scheme 65) was formed. These observations were in agreement with those of Motry *et al.*.[124] They reported that the hydroboration reaction of 1-hexene with benzo-1,3,2-diazaborolane was not successful. Even after refluxing at 100 °C for 1 week, no hexyl-benzo-1,3,2-diazaborolane was formed.



Scheme 65

When comparing benzo-1,3,2-diazaborolane (**19**) to benzo-1,3,2-dithiaborolane (**12**), it can be seen that both reagents show reduced reactivity towards olefins. This is attributed to the fact that for both nitrogen and sulfur substituents a lone pair of electrons is donated to the vacant p-orbital on boron through intramolecular back-donation and in both reagents the aromatic ring acts as a pool of electrons, thus allowing for more back-donation. However, for benzo-1,3,2-dithiaborolane (**12**), the interaction between the

Lewis acidic group B-H and the olefinic double bond can be established at elevated temperatures. Benzo-1,3,2-diazaborolane showed no reaction even at elevated temperatures and extended reaction times. This discrepancy between the two reagents revealed that the magnitude of back-donation is greater for the nitrogen than for the sulfur substituents. These findings are in accordance with those reported by Denk *et al.*,[123] which showed that the magnitude of back-donation decreased in the series $R_2N > RO > F$.[123]

Brown *et al.*[55] reported that benzo-1,3,2-dioxaborolane (catecholborane) hydroborates alkenes at 100 °C in 2 hours, while in this investigation it has been shown that benzo-1,3,2-dithiaborolane (**12**) hydroborates alkenes at 150°C in 3 hours. While its nitrogen analogue benzo-1,3,2-diazaborolane (**19**) does not react with the alkene at all. This reveals the reactivity trend of these reagents towards alkenes. That is, O > S > N (Figure 3.41). This trend decrease with increasing magnitude of back-donation, and it also indicates that the Lewis acidity of the B-H group decreases with increasing magnitude of back-donation.

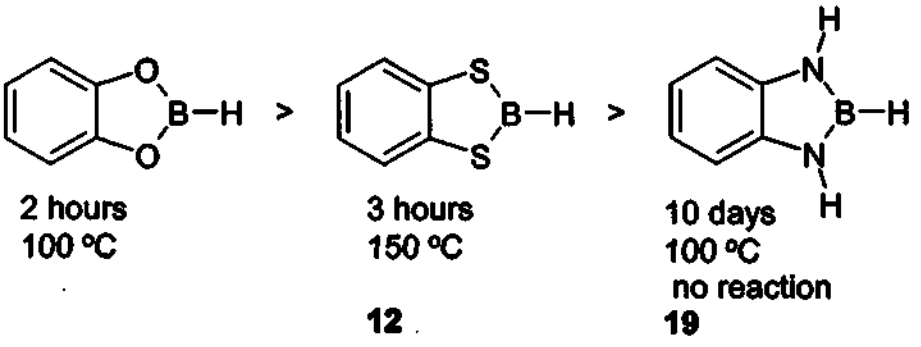


Figure 3.41

The aim to slow down the hydroboration reaction was achieved with the sulfur hydroborating agents, and the results from these reactions are indeed very interesting. Our aim was to slow down the reactions, in addition to evaluate these compounds with respect to their ability to isomerise and displace from the alkene. If one considers the types of compounds that have been synthesised within this study we have a range of

compounds with various electronic and steric features making this an interesting range of species to explore. An obvious problem with the nitrogen analogues is their significantly moderated reactivity. Consequently it was decided to explore possible catalysts for the reaction.

3.7 Hydroboration Reactions Catalyzed by Transition Metal Catalysts

It has been discussed in Chapter 1, Section 1.6 that transition metal systems can enhance the rate of addition of catecholborane to olefins. It has been shown in literature that many hydroboration catalysts simply catalyze decomposition of catecholborane.[87 - 91] Xiaoming *et al.*[85] reported that bis-(cyclopentadienyl) titanium dimethyl (Cp_2TiMe_2) is a true hydroboration catalyst (refer to Chapter 1, Section 1.6.4, page 38) because it does not catalyze decomposition of catecholborane to diborane. Cp_2TiMe_2 was then envisioned as the suitable catalyst for hydroboration of olefins using sulfur and nitrogen hydroborating agents synthesized in this study.

3.7.1 Cp_2TiMe_2 Catalyzed Hydroboration Reactions

3.7.1.1 Introduction

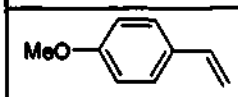
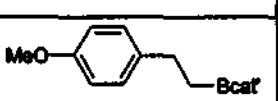
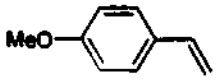
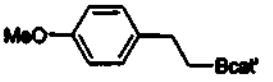
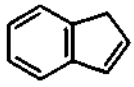
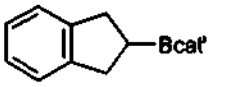
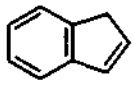
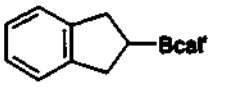
Extensive studies by Xiaoming *et al.* using pure dimethyltitanocene, revealed that no trialkylboronate esters were formed, and this indicated that this catalyst did not catalyze catecholborane decomposition, but catalyzed the hydroboration reaction.[85]

Further mechanistic investigations on this system led to the discovery of titanocene bis(borane) σ–complex ($Cp_2Ti(HBCat)_2$).[125] This compound was derived from the reaction of Cp_2TiMe_2 with excess catecholborane. Hartwig *et al.*[126] observed no reaction between Cp_2TiMe_2 and the alkene in the absence of catecholborane, this observation led to the speculation that bis(borane) complex is the active catalyst in the hydroboration of

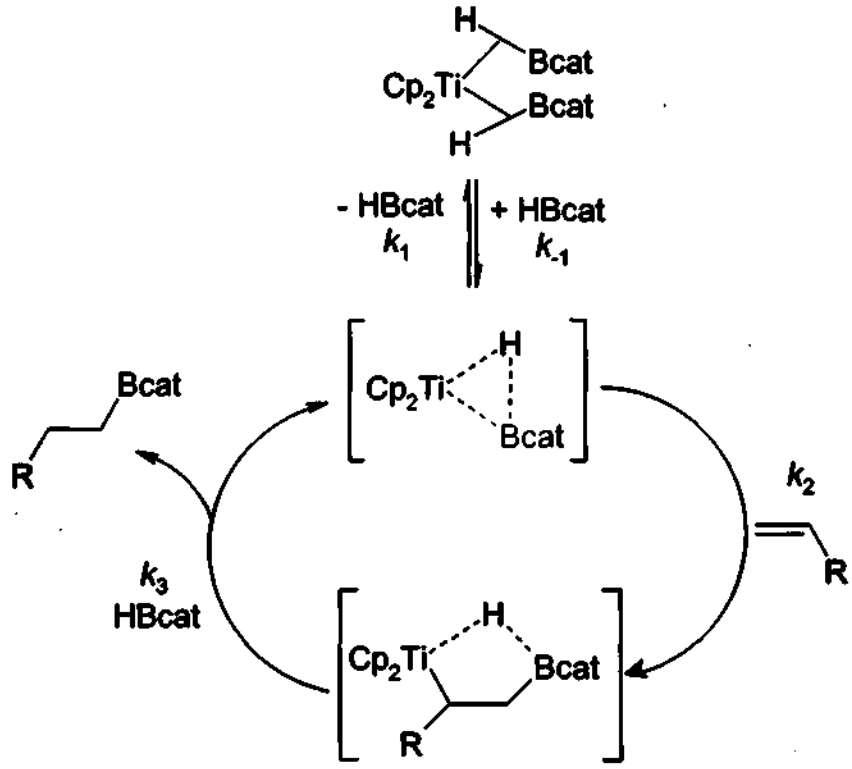
alkenes catalyzed by Cp_2TiMe_2. It was then found that titanocene bis(borane) complex catalyzed hydroboration reactions faster than Cp_2TiMe_2.[126]

Table 3.5 shown below, presents a comparison of reactivities of $Cp_2Ti(HBCat)_2$ and Cp_2TiMe_2. For the bis(borane) complex, indene and *p*-methoxy styrene resulted in a 90 – 100% yield of hydroboration products in 10 minutes, while on the other hand reactions catalyzed by Cp_2TiMe_2 afforded the product in 10 hours. Both reactions led to anti-Markovnikov products.[126]

Table 3.5 Showing the reactivity comparison [126]

Substrate	Catalyst	Conditions	Product	Yield (%)
	$Cp_2Ti(HBcat\text{-}4\text{-}t\text{-}Bu)_2$	10 min 25 °C		90
	Cp_2TiMe_2	10 h 25 °C		96
	$Cp_2Ti(HBcat\text{-}4\text{-}t\text{-}Bu)_2$	10 min 25 °C		100
	Cp_2TiMe_2	10 h 25 °C		96

It has also been reported in this paper that previous reports contradicted their observations of clean hydroboration of alkenes catalyzed by Cp_2TiMe_2 *via* the bis(borane) complex.[126] Hartwig *et al.* then proposed a mechanism of catalyzed hydroboration (Scheme 66) that fitted experimental data, in order to confirm that the bis(borane) complex behaves like a true hydroboration catalyst.[126]

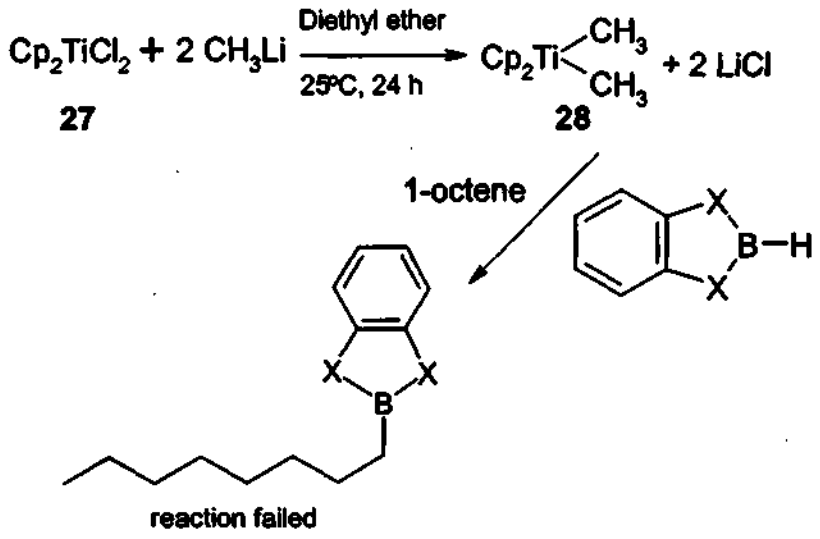


Scheme 66[126]

3.7.1.2 Cp_2TiMe_2 Catalyzed Addition of Benzo-1,3,2-dithiaborolane to 1-Octene

Xiaoming *et al.*, reported that alkenes are hydroborated by mixing the alkene and borane with isolated Cp_2TiMe_2 or generate the catalyst *in situ* prior to addition of alkene and borane.[85] In our study, the catalyst was synthesized in *situ* using the standard procedure reported by Erskine *et al.*[127] Cyclopentadienyl titanium dichloride (27) reacted with methyllithium in a 1:2 stoichiometric ratio in an ethereal solvent at 10 °C in the dark. The formation of Cp_2TiMe_2 (28) after 20 minutes was indicated by the colour change from brick red to orange-brown. Two experiments were conducted concurrently. In the first experiment, the *in situ* prepared Cp_2TiMe_2, 1-octene and benzo-1,3,2-dithiaborolane (12) were injected into a flame dried quartz NMR tube, evacuated and flushed with dry nitrogen. In the second experiment, benzo-1,3,2-diazaborolane (19) was used instead of

(12). In both experiments no octylboronate ester was observed spectroscopically after reacting for 24 hours at 25 °C (Scheme 67).



Scheme 67

The catalyzed hydroboration reaction shown above was attempted several times, the catalyst was freshly prepared for each attempt. However, on no occasion was there any evidence for the reaction occurring. Though Xiaoming *et al.* carried out their experiments[♦] on catecholborane,[85] we were still surprised that we observed no reactions. This discrepancy led to the search for a different transition metal catalyst that would perform the desired hydroboration reactions.

Attention was then focused on the Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) which has been shown in the literature to afford the desired transformations (refer to Chapter 1, Section 1.6.1, page 33). This transition metal complex is known to catalyze hydroboration reactions.

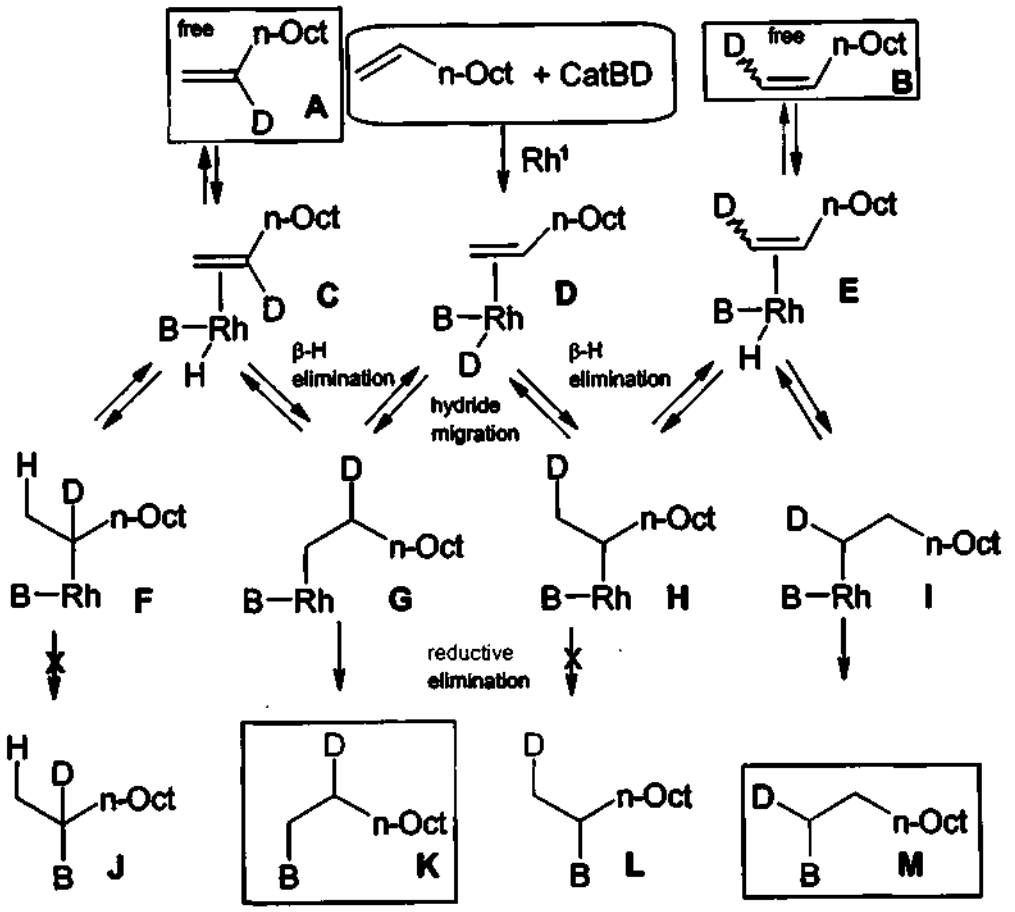
[♦] Refer to Chapter 1, Section 1.6.4.2, page 40 for a summery of experiments carried out by Xiaoming and Hartwig.

3.7.2 $Rh(PPh_3)_3Cl$ Catalyzed Hydroboration Reactions

3.7.2.1 Introduction

Männig and Nöth[79] reported the first example of rhodium catalyzed hydroboration of alkenes in 1985. Furthermore, Evans *et al.*[80] screened a number of other transition metal complexes for catalytic activity in the hydroboration of 1-decene with catecholborane. Their study confirmed that rhodium complexes are the most suitable catalysts for hydroboration. Recently, Evans *et al.*[128] also conducted deuterium labelling studies in order to provide additional information on the mechanism for Rh(I) catalyzed hydroboration initially proposed by Männig and Nöth[79] (refer to Chapter 1, Scheme 43).

From the labelling studies, it was found that deuterium was not only incorporated in the α– and β–carbons of the product alcohol, but also found in the recovered olefins from the reaction of 1-decene with deuteriocatecholborane catalyzed by $Rh(PPh_3)_3Cl$. This interesting observation demonstrated that the mechanism of catalyzed hydroboration was not simple as presented initially by Männig and Nöth. More data was required in order to understand the deuterium/hydride migration step. In this investigation, Evans *et al.*[126] proposed a mechanism that shows six deuterium containing compounds (Scheme 68) that are expected to form if the olefin complexation to rhodium and hydride migration are reversible.



Scheme 68[128]

The above Scheme illustrates seven distinct processes proposed for catalyzed hydroboration of 1-decene:-

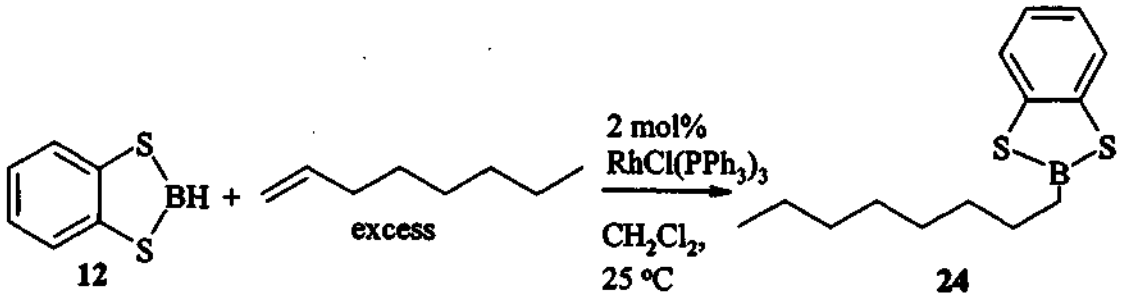
1. **D** to **G**, hydride migration, resulting in the formation of a primary alkylrhodium.
2. **D** to **H**, formation of a secondary alkylrhodium through hydride migration.
3. **G** to **D**, β-hydride elimination of a primary alkylrhodium.
4. **H** to **D**, the elimination of the β-hydride of a secondary alkylrhodium.
5. **G** to **K**, the primary alkylboronate is reductively eliminated.
6. **H** to **L**, the secondary alkylboronate is reductively eliminated.
7. **C** to **A**, alkene decomplexation.

The observed products of the catalyzed hydroboration reaction are enclosed in boxes, compound **L** is not formed due to the fact that reductive elimination of alkylboronate

from secondary alkylrhodium complex is slower than other processes occurring during catalysis. This observation led to the discovery that the passiveness of reductive elimination of compound **H** is the driving force for the high level of regioselectivity found in rhodium catalyzed hydroboration of internal alkenes - about 99 (primary alcohol): 1 (secondary alcohol).[128]

3.7.2.2 $RhCl(PPh_3)_3$ Catalyzed Addition of Benzo-1,3,2-dithiaborolane to 1-Octene

The reaction of benzo-1,3,2-dithiaborolane with 1-octene catalyzed by $RhCl(PPh_3)_3$ (2 mol%) at 25 °C in CH_2Cl_2 (Scheme 69) resulted in an immediate change in colour from brick red to dark green upon mixing of all reagents. After 24 hours the ^{11}B NMR analysis of the product mixture showed an intense singlet at 59.6 ppm (Figure 3.42) attributed to octyl-benzo-1,3,2-dithiaborolane (**24**) (*ca.* 60% yield). The DEPT spectrum of this sample also confirmed the formation of the desired product (**24**) (Figure 3.43). No trialkylboronate ester was detected, this indicated that $RhCl(PPh_3)_3$ did not catalyze decomposition of benzo-1,3,2-dithiaborolane (**12**) to $BH_3{:}SMe_2$.



Scheme 69

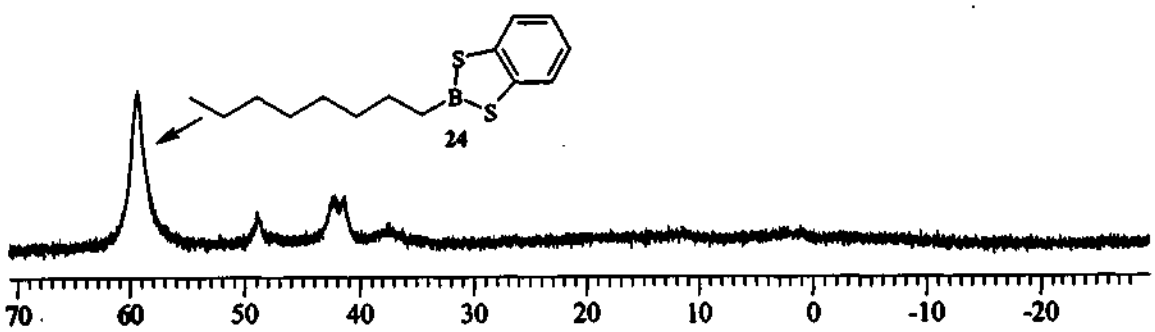


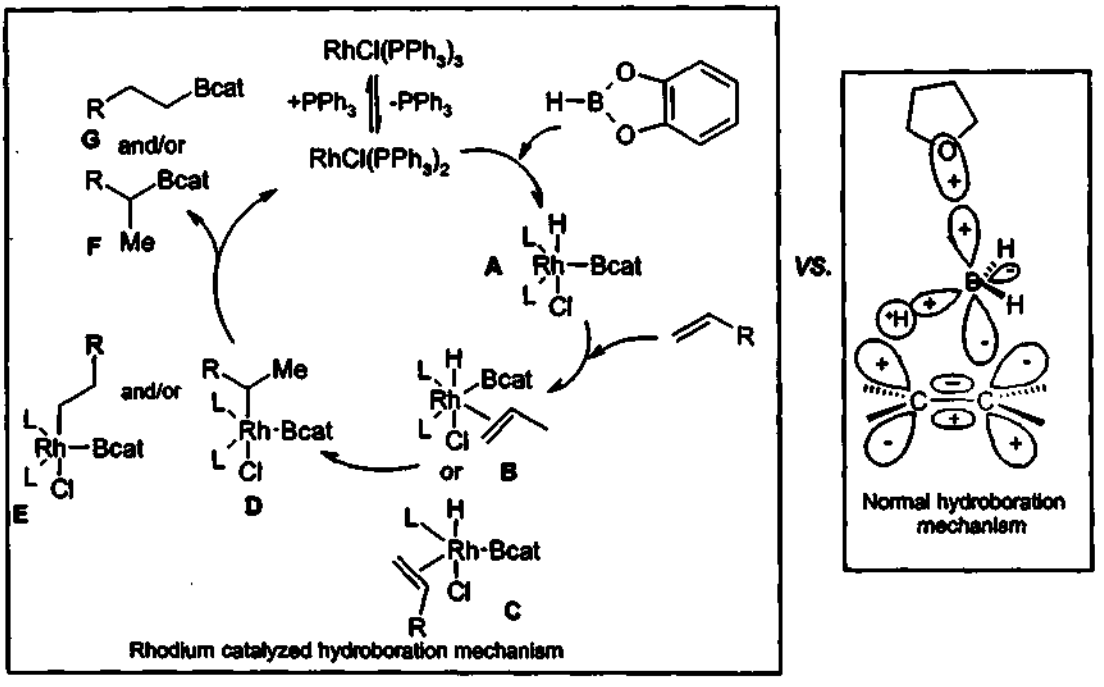
Figure 3.42 ^{11}B NMR spectrum obtained from the catalyzed hydroboration of 1-octene with benzo-1,3,2-dithiaborolane.

This was an interesting, and pleasing observation because it afforded the desired product in high yields at 25 °C. When comparing the uncatalysed reaction (Scheme 63) with the catalysed reaction (Scheme 69), it can be seen that in Scheme 63 the product is obtained after refluxing at 150 °C, at this temperature the product is formed through a normal hydroboration mechanism (refer Chapter 1, Section 1.3.2). In Scheme 69, the octyl-boronate is obtained at 25 °C through a different mechanism, as proposed by Männig and Nöth (Scheme 43) (refer to Chapter 1, Section 1.6.1.1, and page 35).

Scheme 70 shows a comparison of the rhodium catalyzed hydroboration mechanism by Männig and Nöth and the concerted $[_{\pi}2_s + _{\sigma}2_s]$ addition of borane to an alkene reported by Dewar *et al.*.[22] It can be seen that without the catalyst, electrons are required to flow from the π-orbital of the alkene double bond to the empty p-orbital of the boron and also there is a back-donation from the B-H bond to the π*-orbital of the alkene. However, for benzo-1,3,2-dithiaborolane (12), the lone pair of electrons from the sulfur substituents interacts strongly with the empty p-orbital. As a result, it becomes less susceptible to the attack by the electrons from the π-orbital of the alkene, hence slowing the non-catalyzed hydroboration reaction down.

While on the other hand, in the presence of $RhCl(PPh_3)_3$, benzo-1,3,2-dithiaborolane (12) hydroborated 1-octene through a completely different mechanism. In this case the B-H bond is inserted into the coordinatively unsaturated Rh(I) centre, the resulting complex

then coordinates 1-octene, followed by hydride migration. This is then followed by reductive elimination of the primary-octyl-benzo-1,3,2-dithiaborolane (24). The product boronate ester is an *anti*-Markovnikov product because the reductive elimination of the secondary-alkylrhodium complex is very passive.[128]



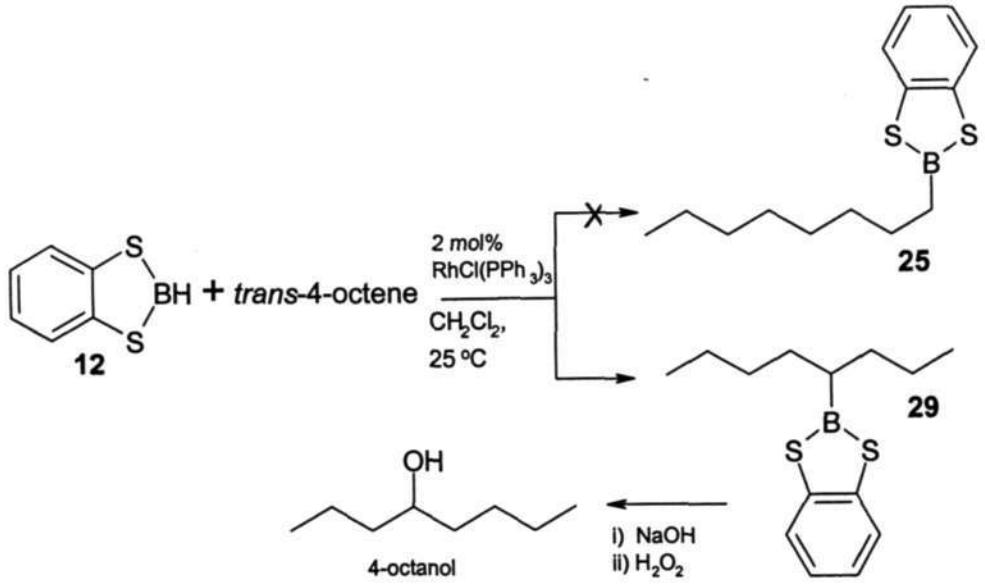
Scheme 70#

3.7.2.3 RhCl(PPh$_3$)$_3$ Catalyzed Addition of Benzo-1,3,2-dithiaborolane to 4-Octene

From the industrial perspective on this project we were interested to explore the catalysed reaction with an internal olefin such as *trans*-4-octene. The internal olefin is more sterically demanding than the terminal olefin and consequently these factors would need to be examined. The reactions were conducted with freshly prepared benzo-1,3,2-dithiaborolane (12) and *trans*-4-octene. A yield of 59% of the octylboronate was observed from the ^{11}B NMR spectroscopic analysis (Figure 3.43) of the product mixture

This Scheme shows a comparison of Scheme 43 from chapter 1, section 1.6.1.1, page 35 and Figure 1.3 from chapter 1, section 1.3.3, page 11.

after 24 hours at 25°C from the catalyzed hydroboration reaction of *trans*-4-octene with (**12**) in the presence of 2% catalyst in CH_2Cl_2.



Scheme 71

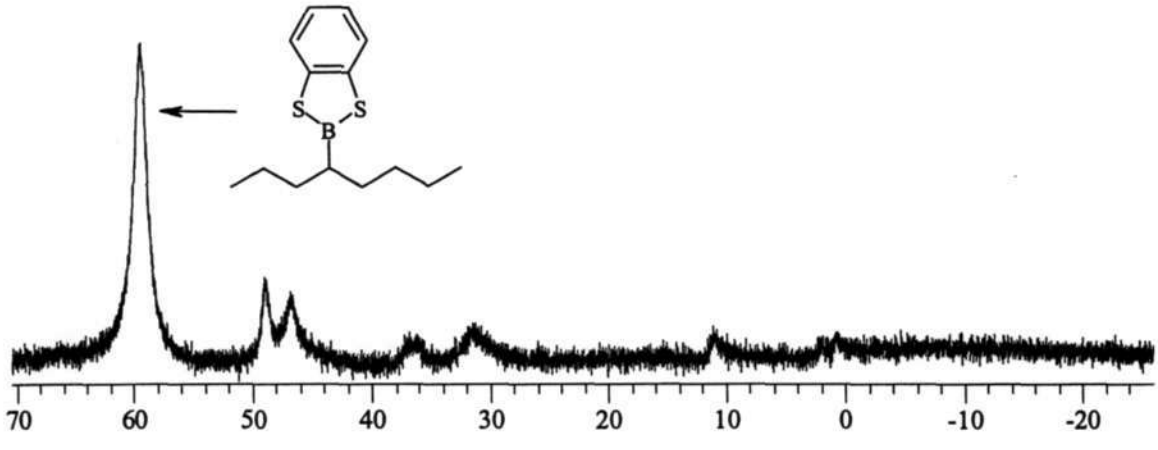


Figure 3.43 ^{11}B NMR spectrum obtained from the catalyzed hydroboration of *trans*-4-octene with benzo-1,3,2-dithiaborolane.

It was expected that the internal octylrhodium complex would isomerize to the primary octylrhodium complex, and this complex would then produce the primary octylboronate ester *via* reductive elimination process. These speculations were made based on the

mechanism (Scheme 68) by Evans *et al.*,[128] which showed that reductive elimination of the secondry alkylrhodium complex is slower than the reductive elimination of the primary alkylrhodium complex.[128] This was thought to be an alternative route to achieving the contrathermodynamic isomerization of internal olefins without refluxing the internal alkylboronate ester at 160 °C.

From the ^{11}B NMR spectrum obtained for this mixture, an intense singlet at 59.8 ppm (Figure 3.43) was obtained. The product formed from the internal olefin resonated at the chemical shift similar to that given by the terminal olefin. As a result, it was not possible to predict if the product was an internal or terminal octylboronate. The DEPT spectrum showed the internal octylboronate and no terminal boronate ester. These results were not sufficient to lead to the conclusion about this system; consequently an oxidative-workup of the product mixture was conducted. ^{1}H NMR spectroscopic analysis displayed a singlet at 4.7 ppm corresponding to the -OH proton and a multiplet at 3.6 ppm attributed to proton bonded to C_4 bearing the –OH group. GC-MS analysis confirmed that only 4-octanol was produced.

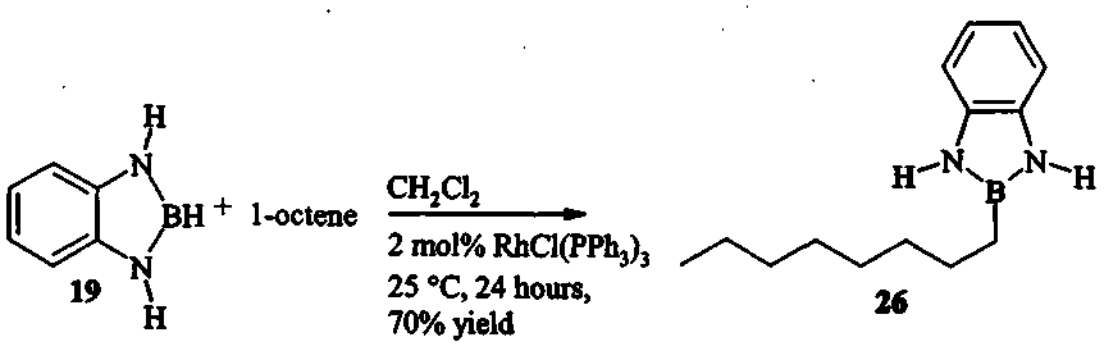
Our observations are in agreement with those reported by Evans *et al.*, only 4-octanol was produced in the hydroboration of *trans*-4-octanol with catecholborane catalyzed by $RhCl(PPh_3)_3$.[128] Evans *at al.* also reported that the absence of the regioisomeric alcohols is an indication that isomerization does not occur under these conditions,[128] and this led to the conclusion that for *trans*-4-octene, the hydride migration is irreversible. This was in contrast with the mechanism proposed for 1-decene that the hydride migration is reversible. It was then proposed that β-hydride elimination process is sensitive to the steric requirements of the alkene being produced; i.e., for 1-decene, the formation rhodium-terminal alkene complex is faster while in *trans*-4-octene, the formation of rhodium-internal alkene complex is less facile relative to reductive elimination.[128]

3.7.2.4 $RhCl(PPh_3)_3$ Catalyzed Addition of 4,7-Dichloro-1,3,2-benzodithiaborolane to 1-and 4-Octene

For the 4,7-dichloro-1,3,2-benzodithiaborolane (**14**) systems, no hydroboration products were formed. ^{11}B NMR spectroscopy showed significant decomposition of the hydroborating agent for both 1-and 4-octene catalyzed hydroboration reactions. No trialkylboronate esters were detected spectroscopically, this indicated that 4,7 dichloro-1,3,2-benzodithiaborolane did not break down to BH_3 but decomposed to non-hydroborating species.

3.7.2.5 $RhCl(PPh_3)_3$ Catalyzed Addition of Benzo-1,3,2-diazaborolane to 1-Octene

The Wilkinson's catalyst demonstrated a high catalytic activity when it catalyzed the hydroboration of 1-octene with benzo-1,3,2-diazaborolane (**19**) at 25°C which has been shown from the early studies to be unreactive even after 10 days reflux.[122] The ^{11}B NMR spectroscopy displayed a new singlet at 31.6 ppm (Figures 44.3 and 45.3A) attributed to the terminal octyl-benzo-1,3,2-diazaborolane (**26**) (Scheme 72), about 70% yield of octyl-benzo-1,3,2-diazaborolane (**26**) was formed after 24 hours. No disproportionation of benzo-1,3,2-diazaborolane (**19**) was observed, unlike benzo-1,3,2-dithiaborolane (**12**) where small disproportionation fragments were observed. As a result the yields were slightly higher than those obtained from benzo-1,3,2-dithiaborolane (**12**).



Scheme 72

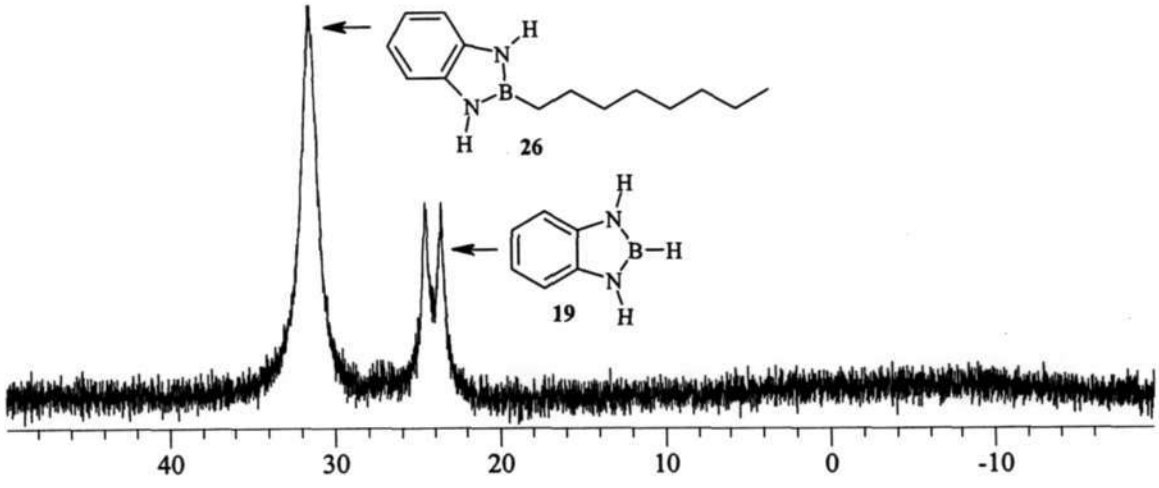


Figure 3.44 ^{11}B NMR spectrum obtained from the catalyzed hydroboration of 1-octene with benzo-1,3,2-diazaborolane after 19 hours at 25 °C.

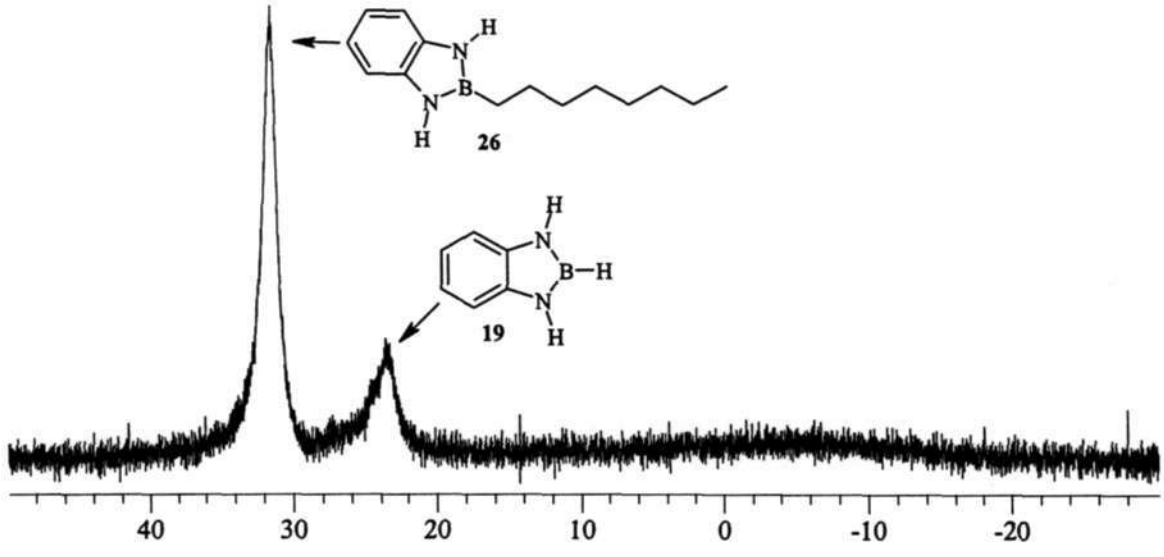


Figure 3.45A ^{11}B NMR spectrum obtained from the catalyzed hydroboration of 1-octene with benzo-1,3,2-diazaborolane after 24 hours at 25 °C.

The formation of the octyl-benzo-1,3,2-diazaborolane was also confirmed by the MS analysis of the product mixture, which showed an intense peak at 9.59 min containing a molecular ion with a ratio of 230.3 *m/z* with 100% abundance (Figure 3.45B). This molecular ion was assigned to the product octyl-1,3,2-dithiaborolane (26) (Mw = 230.2 g/mol).

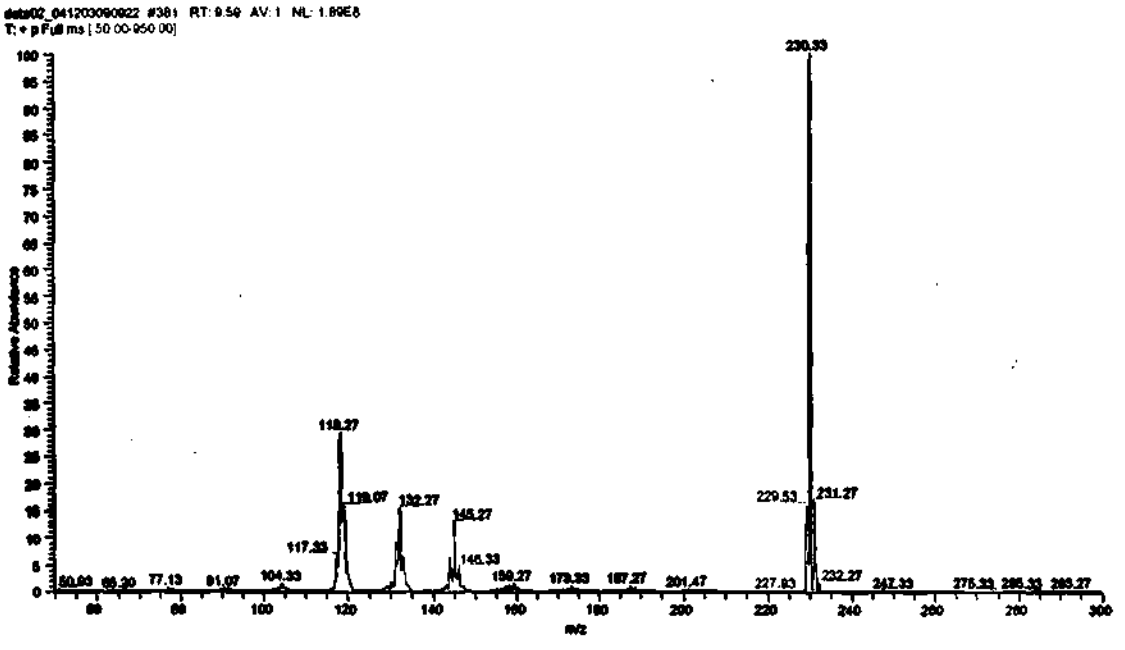
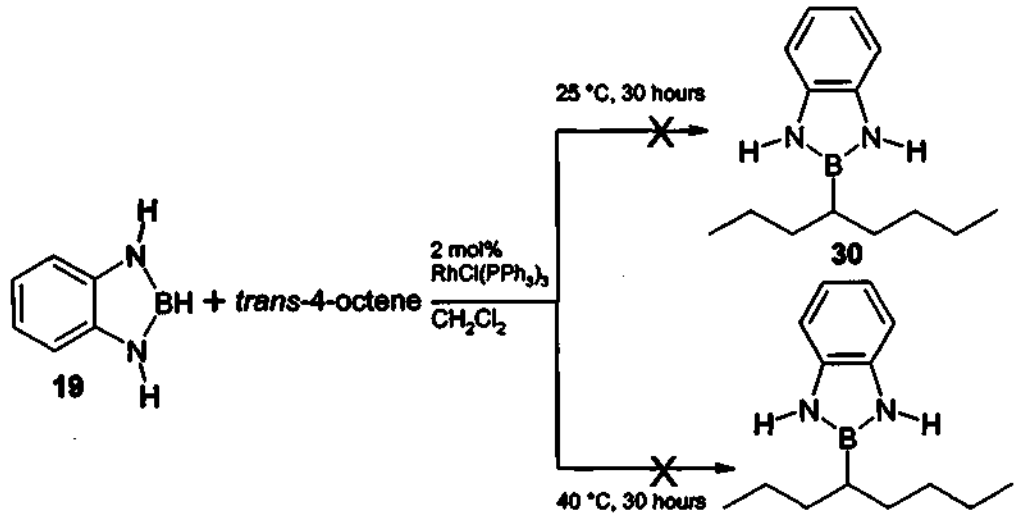


Figure 3.45B The MS trace of octyl-1,3,2-diazaborolane (26)

3.7.2.6 $RhCl(PPh_3)_3$ Catalyzed Addition of Benzo-1,3,2-diazaborolane to 4-Octene

This case is slightly different from other cases presented above. Here the hydroborating agent has a higher steric requirement than benzo-1,3,2-dithiaborolane (12) or catecholborane and the *trans*-4-octene also has a higher steric requirement than 1-octene. It was speculated that increasing the steric demand of the hydroborating agent would promote the isomerization of the rhodium-internal alkene complex in order to achieve the primary alkyboronate as the major product unlike the case of the less sterically demanding benzo-1,3,2-dithiaborolane (12) or catecholborane with *trans*-4-octene where only 4-octanol was produced.

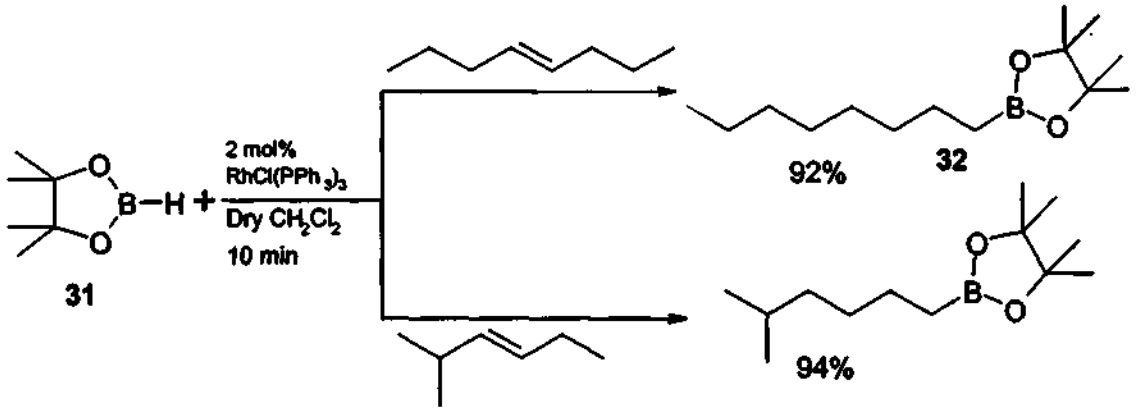
The ^{11}B NMR analysis of the product mixture from the catalyzed hydroboration of *trans*-4-octene with (19) (Scheme 73) showed only a doublet at 23.9 ppm for the B-H coupling in the starting hydroborating agent (19). It was clear from the NMR analysis that no hydroboration reaction product was formed. No hydroboration was observed even after heating the mixture at 40 °C for 30 hours.



Scheme 73

Failure to hydroborate *trans*-4-octene with benzo-1,3,2-diazaborolane (19) under catalytic conditions was attributed to the sterically demanding structure of (19) during the initial boron-rhodium complex. This observation was in contrast to the successful regioselective catalytic hydroboration of *tran*-4-octene with catecholborane[128] and benzo-1,3,2-dithiaborolane. Thus, these results indicate the fine balance required between having sufficient steric bulk to promote isomerisation, and too much bulk and thus preventing the formation of the initial rhodium-boron complex.

Recently, Pereira and Srebnik[129] successfully used Rh(I) to catalyze the hydroboration of alkenes with pinacolborane (31) which was previously reported by Tucker *et al.*[130] to be unsuccessful. 100% terminal octylpinacolboronate (32) was obtained during the $RhCl(PPH_3)_3$-catalyzed hydroboration of *trans*-4-octene (Scheme 74). In this study, very fast reaction times were reported, about 10 minutes at 25 °C.[129]



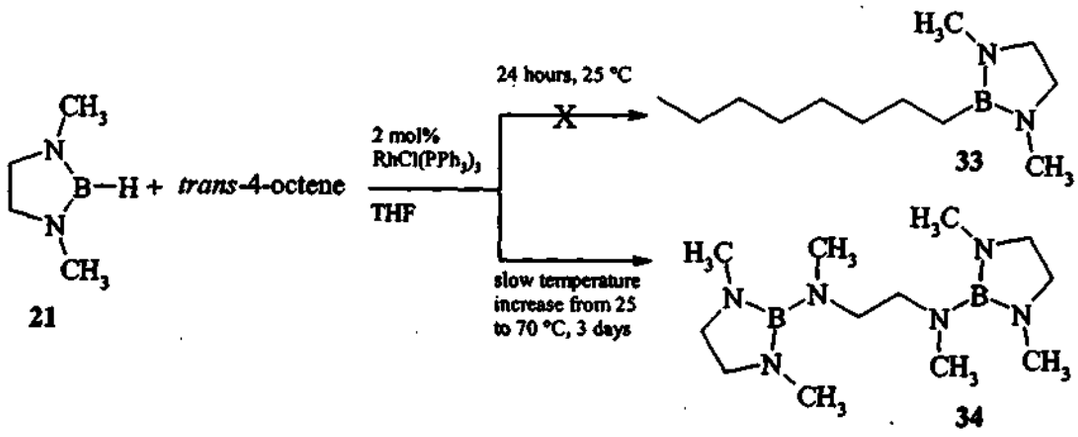
Scheme 74

For *cis*-2-methyl-3-hexene, the boron atom isomerized to the non branched carbon, while on the other hand catecholborane gave the expected internal boronate.[129] Pereira and Srebnik attributed the difference between the pinacolborane and catecholborane to the higher steric requirement of pinacolborane, which causes a fast β-hydride elimination/ recomplexation sequence. This leads to the placement of the rhodium on the least hindered carbon, followed by a slow boron insertion. The resulting terminal pinacol alkylborane (32) can be displaced to generate the desired α-olefin.

From the perspective of this study, these findings supported the initial idea proposed for an alternative route for contrathermodynamic isomerization of internal olefins, and thus motivated us to pursue this study using a nitrogen-based hydroborating reagent with close resemblance to pinacolborane.

3.7.2.7 $RhCl(PPh_3)_3$ Catalyzed Addition of 1,3-Dimethyl-1,3,2-diazaborolane to 4-Octene

In this study, 1,3-dimethyl-1,3,2-diazaborolane (**21**) was used instead of pinacolborane. In (**21**) the steric hindrance is shifted closer to the boron atom. No hydroboration product was obtained after 1 day from the reaction of *trans*-4-octene with 1,3-dimethyl-1,3,2-diazaborolane (**21**) catalyzed by $RhCl(PPh_3)_3$ at 25 °C (Scheme 75)



Scheme 75

It was thought that slow elevation of the reaction temperature would assist the catalyzed hydroboration of *trans*-4-octene. However, it was found that at 70 °C 1,3-dimethyl-1,3,2-diazaborolane (**21**) disproportionated to *N,N'*-bis-(1,3-dimethyl-[1,3,2]diazaborolidin-2-yl)-*N,N'*-dimethyl-ethane-1,2-diamine (**34**) which gave an intense singlet at 24.0 ppm (Figure 3.46). Failure of 1,3-dimethyl-1,3,2-diazaborolane (**21**) to hydroborate *trans*-4-octene under catalytic conditions was attributed to the fact that the methyl substituents of the nitrogen groups are too close to the boron, thus hindering the boron atom from interacting with rhodium. These findings were consistent with those found using benzo-1,3,2-diazaborolane (**19**).

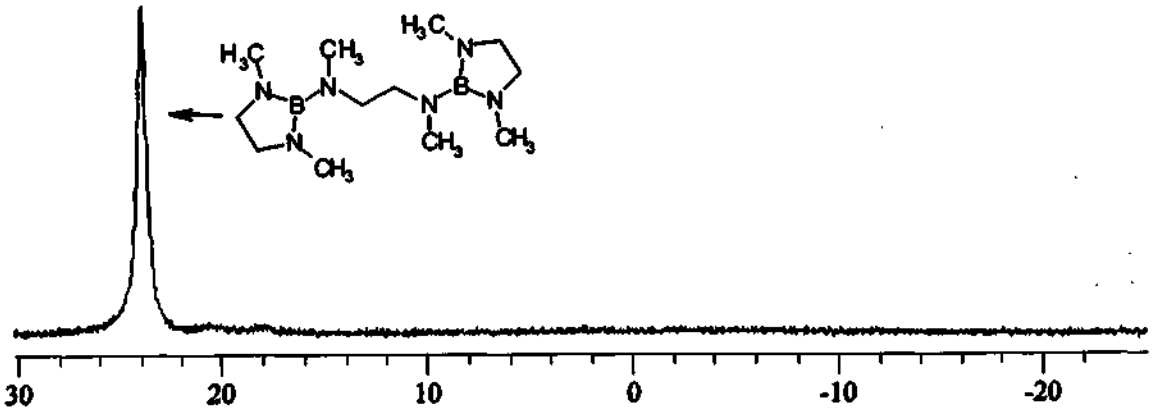


Figure 3.46 ^{11}B NMR spectrum obtained from the catalyzed hydroboration of *trans*-4-octene with 1,3-dimethyl-1,3,2-diazaborolane at 70 °C.

3.7.2.8 $RhCl(PPh_3)_3$ Catalyzed Addition of 1,3-Dimethyl-1,3,2-diazaborolane to 1-Octene

From the results of the catalyzed reaction of 1,3-dimethyl-1,3,2-diazaborolane (21) with *trans*-4-octene discussed above, it was not clear if the steric hindrance was caused by the hydroborating agent (21) or *trans*-4-octene, resulting in the failure of the catalyzed reaction. Less sterically demanding 1-octene was used instead of *trans*-4-octene, and the same reaction conditions were employed. No hydroboration product was detected spectroscopically. *N,N'*-bis-(1,3-dimethyl-[1,3,2]diazaborolidin-2-yl)-*N,N'*-dimethyl-ethane-1,2-diamine (34) was detected at elevated temperatures.

This data indicated that the steric hindrance is caused by 1,3-dimethyl-1,3,2-diazaborolane (21) only not the olefin under investigation. The high steric requirement of (21) prevents the oxidative addition of the B-H bond across the coordinatively unsaturated Rh (I) metal centre. This is the first step of the catalytic cycle, absence of this step leads to failure of the alkene insertion step. As a result, hydroboration will not occur.

It was thought that 1,3-dimethyl-1,3,2-diazaborolane (21) can be tuned to be a suitable reagent that achieves terminal octylboronate esters; this can be done by replacing the

methyl groups with hydrogen atoms. Before attempting the tuning studies, it was thought that it could be worth repeating the experiment by Pereira and Srebnik[129] in order to find out if hydroboration does take place under these conditions since this was the only article with such findings.

3.7.2.9 $RhCl(PPh_3)_3$ Catalyzed Addition of Pinacolborane to *trans*-4-Octene

$RhCl(PPh_3)_3$ was allowed to catalyze the hydroboration of *trans*-4-octene with pinacolborane at 25 °C, this reaction was conducted in a flame dried quartz NMR tube in order to monitor the progress of the catalyzed hydroboration reaction (Scheme 74). No reaction was observed after 10 minutes which contradicts results by Pereira and Srebnik.[129] After 24 hours, ^{11}B NMR analysis showed a doublet at 28.5 ppm attributed to B-H coupling of pinacolborane (Figure 3.47), a singlet 22 ppm which was attributed to the disproportionation product, this signal was originally present in the stock solution of pinacolborane before addition of the catalyst and the olefin. A broad singlet at 23 ppm was also present in the stock solution.

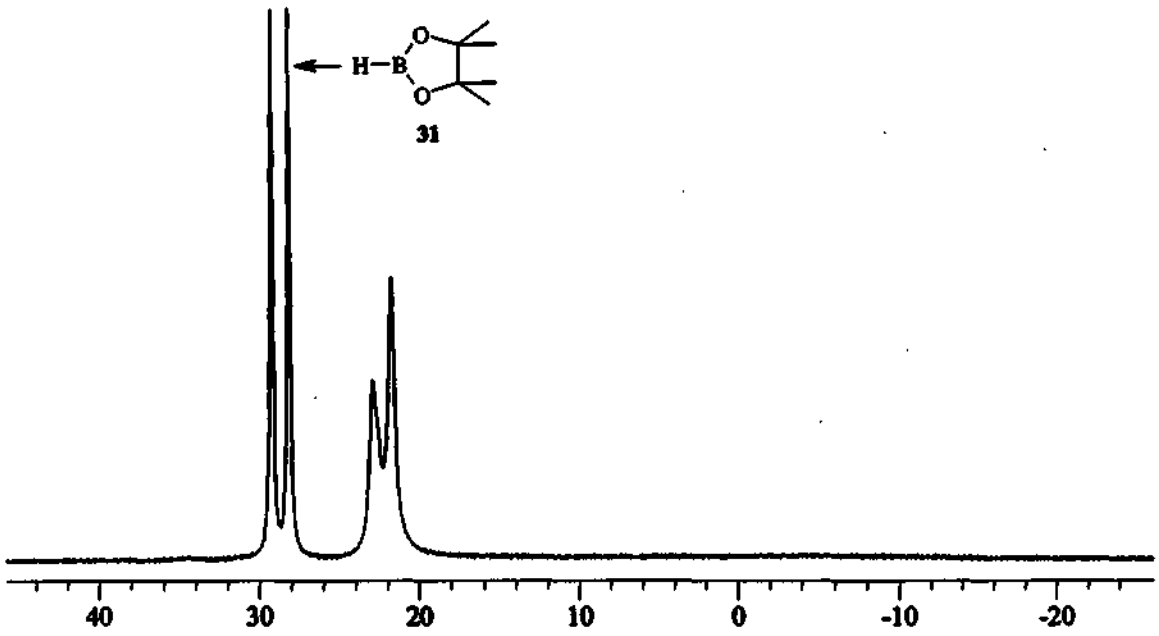
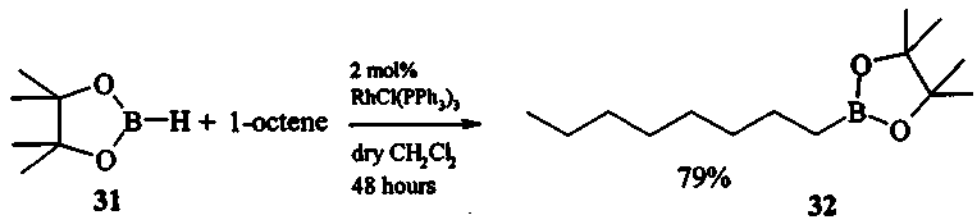


Figure 3.47 ^{11}B NMR spectrum obtained from the reaction pinacolborane and 4-octene after 24 hours at 25 °C in the presence of rhodium catalyst.

These findings were very different from those reported by Pereira and Srebnik.[129] According to the above observations, it was clear that pinacolborane is similar to 1,3-dimethyl-1,3,2-diazaborolane (**21**) in terms of steric hindrance, thus it is unable to hydroborate *trans*-4-octene. This was consistent with previous observations on attempted reactions of benzo-1,3,2-diazaborolane and 1,3-dimethyl-1,3,2-diazaborolane with *trans*-4-octene.

3.7.3.0 $RhCl(PPh_3)_3$ Catalyzed Addition of Pinacolborane to 1-Octene

The reaction of a less sterically demanding 1-octene with pinacolborane in the presence of $RhCl(PPh_3)_3$ indicated the formation of 11% of octyl-pinacol-boronate ester (**32**) after 30 minutes at 25 °C (Scheme 76), characterized by a broad singlet at 34.3 ppm (Figure 3.48) in the ^{11}B NMR spectrum.



Scheme 76

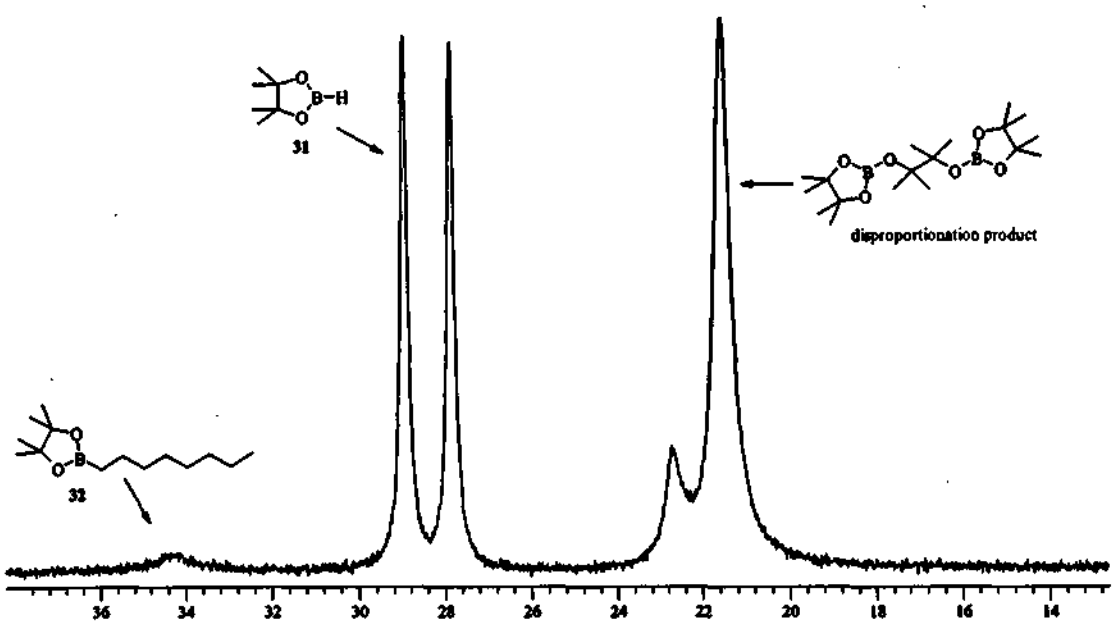


Figure 3.48 ^{11}B NMR spectrum, showing the formation of (32) after 30 minutes.

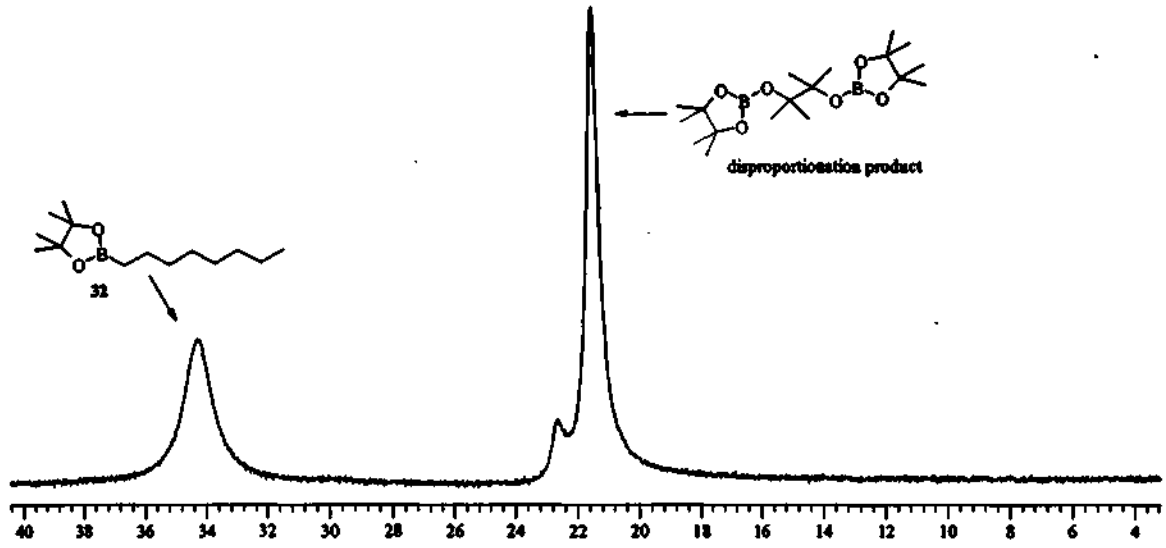


Figure 3.49 ^{11}B NMR spectrum showing complete conversion of pinacolborane forming (32).

These observations indicated that this was a slow reaction. Our observations were in contrast with those reported by Pereira and Srebnik, whose reaction went to completion in 10 minutes.[127] This reaction was allowed to proceed for 48 hours, leading to the formation of *ca.*79% of the terminal octyl-pinacol-boronate ester (**32**) (Figure 3.49). These findings supported the fact that failure of $RhCl(PPh_3)_3$ to catalyse hydroboration of *trans*-4-octene with pinacolborane was due to the steric hindrance.

3.8 Conclusions

The initial aims of this project, to design and synthesize sulfur- and nitrogen-based boranes with a single site available for hydroboration and to evaluate their reactivity towards selected alkenes have all been achieved.

^{11}B NMR spectroscopic technique has been effectively employed in analyzing the boranes as well as to monitor the progress of the hydroboration process. This technique has proved to accurately monitor and quantify the reaction. The *in situ* ^{11}B NMR spectroscopic analysis showed that disproportionation products are also formed during synthesis of the oxygen- and sulfur-based borolanes and not with the nitrogen-based borolane. These interesting results have been rationalized by a computational modelling study. Kinetic and thermodynamic parameters for 1,3,2-dithiaborolane and 1,3,2-dithiaborinane have shown that the sulfur heteroatom interacts with the boron atom, thus reducing the reactivity of these borolanes. The reactivity of the aromatic derivatives of oxygen-, sulfur-, and nitrogen-based boranes decreased with increasing magnitude of back donation as follows: benzo-1,3,2-dioxaborolane > benzo-1,3,2-dithiaborolane >> benzo-1,3,2-diazaborolane.

It was shown that the hydroboration of 1-octene with stable aromatic borolanes such as benzo-1,3,2-dithiaborolane and benzo-1,3,2-dithiaborolane, can be achieved through an alternative mechanism by the use of the Wilkinson's catalyst.

3.9 Future Work

The results obtained in this study have identified various areas for future investigation, including the following:-

- A more complete molecular modelling study focused towards understanding other factors leading to disproportionation of the oxygen- and the sulfur-based boranes. This may be achieved by modelling the intermediate species. Modelling studies may also shed light in the understanding of the interaction of a range of borolanes with selected alkenes. This may assist in the rationale design of a suitable catalytic system for this process.

- Possible studies into the kinetics between the sulfur compounds (i.e. 1,3,2-dithiaborolane and 1,3,2-dithiaborinane) and different types of alkenes could form the basis of another study as very little data exists in the literature and such data would be of scientific merit.

- To investigate the role of other catalytic systems as well as the potential impact of a tethered catalyst approach, which may be of interest in an industrial process.

- The chemistry, of the nitrogen containing borolanes should be further investigated in terms of its applications in synthetic chemistry i.e. its regioselectivity and possible extension into asymmetric hydroboration type reactions, which to date has not been investigated by any other research groups.

Chapter 4.

Experimental

4. EXPERIMENTAL

Synthesized compounds were characterized by ^{11}B NMR spectroscopy (as discussed in the previous section) because it is more definitive as opposed to ^{1}H NMR spectroscopy. This technique has been used by others in the group[115, 116, 117] and was found sufficient to identify the compounds. The use of the MS to characterize the sulfur compounds was not feasible due to the corrosiveness and instability of these compounds within the MS, but the same is not true for the nitrogen compounds.

4.1 General

All glassware was thoroughly dried overnight in an oven at *ca.* 150°C overnight. The glassware was further flame-dried by heating with a hot air gun under reduced pressure and allowed to cool under a stream of dry nitrogen, which was passed through a mixture of silica gel and 0.4 nm molecular sieves just prior to use. Glass syringes, cannulae, and needles were oven dried and stored in a desiccator (charged with a mixture of silica gel and 0.4 nm molecular sieves) prior to use. Disposable syringes and needles were stored in the dessicator before use, and they were discarded after single use. On assembling the glassware, all joints were wrapped with Teflon® tape, and were subsequently sealed with a Parafilm "M"® to ensure a closed system.

All ^{1}H, ^{13}C, DEPT and ^{11}B NMR spectra were recorded on a Varian Unity-Inova 160 MHz spectrometer with a Sun Microsystems, Solaris™ 8 software suite. ^{1}H NMR spectra were recorded in $CDCl_3$ and were referenced using the residual chloroform signal at 7.25 ppm. All ^{11}B NMR spectra were referenced to BF_3:OEt_2 as an external standard (0 ppm) contained within a sealed capillary insert. ^{11}B spectroscopy was utilised in order to identify the compounds as well as to monitor the progress of the reactions. ^{13}C and DEPT (135) spectroscopy were used to identify the hydroboration products. Quartz NMR tubes (5 cm) were used for the ^{11}B NMR spectroscopic experiments and were all oven dried and flushed with dry nitrogen and sealed with a rubber septum prior to injection of the sample or reagents.

GC-MS analysis and ^{1}H NMR spectroscopy were used to identify the alcohols produced after oxidative work up of the product mixture with alkaline peroxide. GC-MS analyses were performed on a Thermofinnigan® (GC) coupled with a PolarisQ® (MS) system operated by the Xcalibur™ software.

Low temperature synthetic reactions were conducted in a Cryostat (Figure 4.1) loaded with isopropanol as the cooling solvent and an immersible stirrer. High temperature reactions were conducted using an aluminium heating block (Figure 4.2) with six NMR tube slots and a thermometer slot, this block was then immersed in a silicon oil bath which is set to the desired temperature.

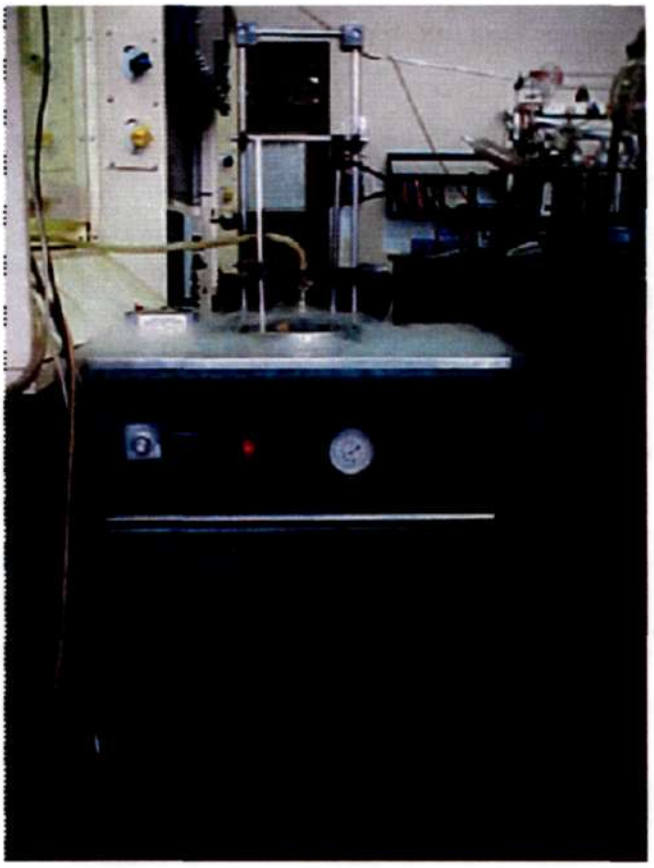


Figure4.1 The Cryostat containing a reaction flask, which is connected to the nitrogen gas line located in the fume cupboard

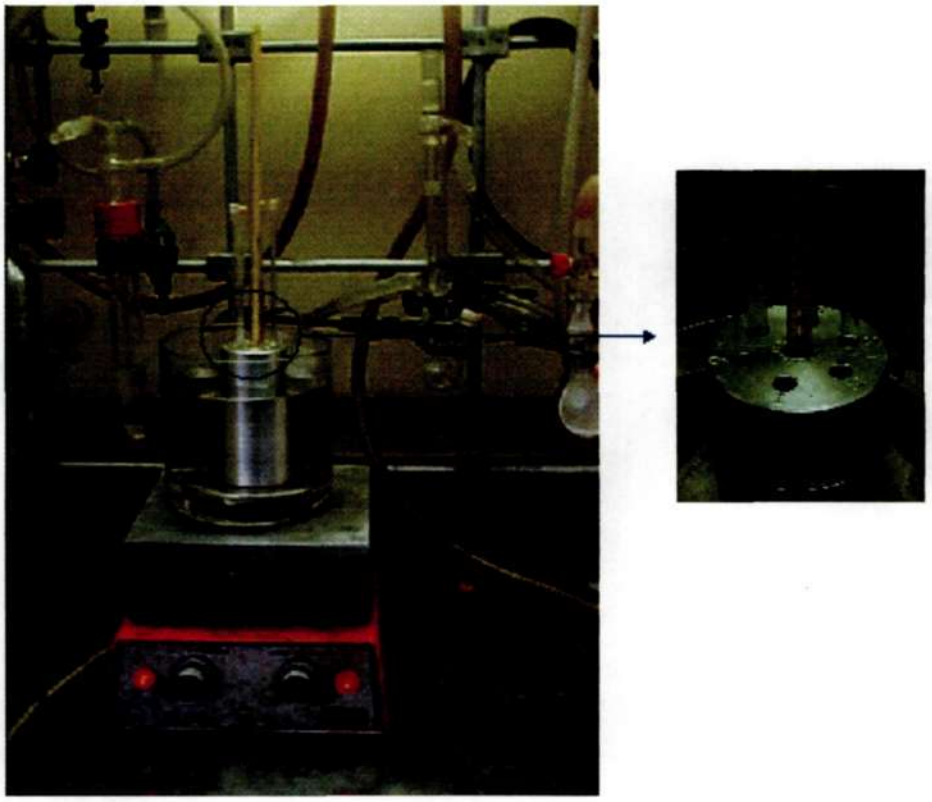


Figure 4.2 Heating block containing quartz NMR sample tubes and a thermometer, the heating block is immersed in hot silicon oil. On the right, is shown a top surface of the heating block.

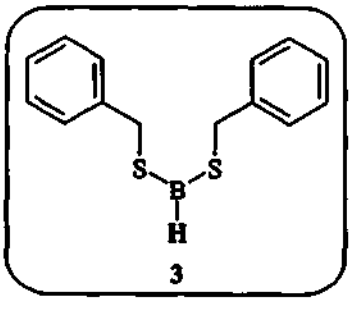
Dry nitrogen gas used in this research was obtained from Afrox as HP grade and subsequently dried through two drying tubes each containing a mixture of molecular sieves and silica gel. All solvents were purified by distillation and dried prior to use.[119] CH_2Cl_2 was distilled over P_2O_5 under dry nitrogen; THF, benzene, diglyme, 1-octene, and *trans*-4-octene were all distilled over sodium wire in the presence of an indicator benzophenone. The solvents were distilled and transferred *via* cannula to a flame-dried, nitrogen flushed flask containing 0.4 nm molecular sieves (activated in the furnace at 600 °C and cooled under dry nitrogen) prior use.

BH_3:SMe_2, 1,2-benzenedithiol, isopropanol, ethanethiol, 3,6-dichloro-1,2-benzenedithiol, *N,N'*-dimethyl-1,2-diaminoethane, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Tris-(triphenylphosphine)-rhodium(I)-chloride, and methyllithium were obtained from Sigma-

Aldrich Co and used without further purification. 1,2-Ethanedithiol, 1,3-propanedithiol, and 1,2-phenylenediamine were obtained from Merck-Schuchardt and used without further purification. Bis(cyclopentadienyl) titanium dichloride was obtained from Strem Chemicals, NaOH from CJ-Chem, benzyl mercaptan from Fluka Chemika, and all these reagents were used without further purification. 1,2-Ethanediol was obtained from Sigma-Aldrich Co., this compound was purified by distillation under dry nitrogen and stored over 0.4 nm molecular sieves.

4.2 Synthesis of Sulfur-Containing Boranes

4.2.1 Synthesis of bis(benzylthio)borane (3)



3

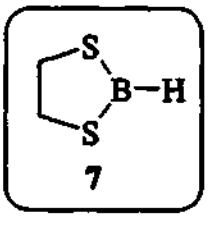
Borane-tetrahydrofuran solution (1M, 2.00 ml, 2.0 mmol) was added to a flame-dried, nitrogen-flushed 10 ml two necked round-bottomed flask. The contents of the flask were cooled to 0 °C in an ice-water bath. Benzyl mercaptan (0.50 ml, 4.0 mmol) was added dropwise *via* a syringe through a rubber septum. The resulting mixture was stirred at room temperature overnight to afford bis(benzylthio)borane (3) (34%) as a clear liquid δ_B (160 MHz; BF_3:OEt_2) = -8.3 ppm, d, J_{B-H} = 159.6 Hz[¶]

[¶] Mass spectrometric data for the sulfur containing compounds was not able to be obtained due to the corrosive nature of the compound and its instability within the instrument.

4.2.2 Synthesis of bis(isopropylthio)- and (ethylthio)boranes

In this section, two experiments were conducted concurrently. Two, flame-dried round bottoned flasks (**A** and **B**) were charged with BH_3:SMe_2 complex in CH_2Cl_2 (5.0 ml, 5.0 mmol), and sealed with tight rubber septa. The contents of both flasks were cooled to 0°C. In flask **A** was syringed isopropyl mercaptan (0.93 ml, 10 mmol) through the rubber septum and in flask **B** was placed ethyl mercaptan (0.74 ml, 10 mmol). The two reaction mixtures were allowed to warm up to room temperature while stirring under dry nitrogen atmosphere. The products obtained from both flasks indicated the formation trimeric species as major products. Flask **A** indicated isopropylthioborane (67%), δ_B (160 MHz; BF_3:OEt_2) = -15.8 ppm, t, J_{B-H} = 120.8 Hz; bis(isopropylthio)borane (10%), δ_B (160 MHz; BF_3:OEt_2) $\delta^{11}B$ = 60.8 ppm, d, J_{B-H} = 145.3 Hz; tris(isopropylthio)borane δ_B (160 MHz; BF_3:OEt_2) = 58.6 ppm, s. Contents of flask **B** displayed results similar to those obtained from flask **A** with negligible differences.

4.2.3 Synthesis of 1,3,2-dithiaborolane (7)

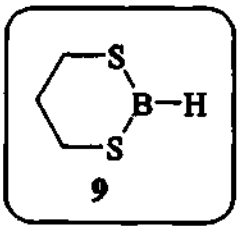


7

Following a modification to the procedure described by Egan *et al.*[118] Borane-dimethyl sulfide complex in CH_2Cl_2 (5.0 ml, 5.0 mmol) was transfered into a flame-dried, nitrogen purged 25 ml two necked round-bottomed flask. The contents of the flask were subsequently cooled to -84 °C in a liquid nitrogen/ethyl acetate slurry, following which a solution of 1,2-ethanedithiol (471 mg, 5.0 mmol) in CH_2Cl_2 (3 ml) was added dropwise to the stirred flask. The reaction mixture was subsequently stirred for 30 min at -84 °C and allowed to warm up to -60 °C. The flask was then transferred to the cryostat, and

allowed to stir for 14 hours at -55 °C under dry atmosphere of nitrogen to afford a clear liquid comprising a mixture of 1,3,2-dithiaborolane (7) (58%) and 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8) (40%). δ_B (160 MHz; BF_3:OEt_2) = 60.5 ppm, d, J_{B-H} = 156.4 Hz; 2,2'-(ethylenedithio)bis-(1,3,2-dithiaborolane) (8) (40%), δ_B (160 MHz; BF_3:OEt_2) = 64 ppm, s; BH_3:SMe_2 (2%), δ_B (160 MHz; BF_3:OEt_2) = 20.5 ppm, q, J_{B-H} = 105.5 Hz.

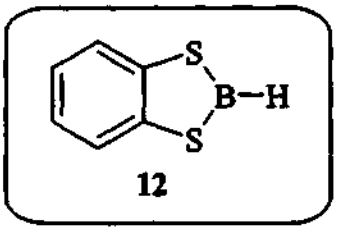
4.2.4 Synthesis of 1,3,2-dithiaborinane (9)



9

Borane-dimethyl sulfide complex in CH_2Cl_2 (1.0 M, 5.0 ml, 5.0 mmol) was stirred at 0 °C under a nitrogen atmosphere. 1,3-Propanedithiol (0.50 ml, 5.0 mmol) was added drop wise over a period of 10 min. The resulting mixture was allowed to stir at room temperature for 7 days to afford a cloudy liquid of 1,3,2-dithiaborinane (9) (35%) δ_B (160 MHz; BF_3:OEt_2) = 55.2 ppm, d, J_{B-H} = 145.8 Hz; and 2,2'- (propylenedithio)bis-(1,3,2-dithiaborinane) (10) (55%), δ_B (160 MHz; BF_3:OEt_2) = 56.6 ppm, s; BH_3:SMe_2 (3%), δ_B (160 MHz; BF_3:OEt_2) = -20.5 ppm, q, J_{B-H} = 105.5 Hz; $HSCH_2CH_2SBH_2$ (7%), δ_B (160 MHz; BF_3:OEt_2) = -16.9 ppm, t, J_{B-H} = 122.3 Hz).

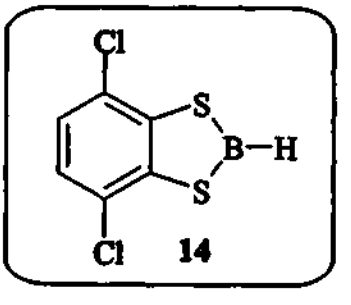
4.2.5 Synthesis of benzo-1,3,2-dithiaborolane (12)



12

1,2-Benzenedithiol (11) (497 mg, 3.50 mmol) in CH_2Cl_2 (5 ml) was added to a stirred solution of borane-dimethyl sulfide complex in CH_2Cl_2 (1.0 M, 3.50 ml, 3.50 mmol) at 25 °C. The reaction was mild with no observable liberation of hydrogen gas. The reaction mixture was allowed to stir for 24 hours at room temperature to afford the desired product benzo-1,3,2-dithiaborolane (12) as a light yellow liquid in quantitative yield, = 53.4 ppm, d, 162.6 Hz). Proton noise decoupling was carried out with subsequent collapse of the doublet to the expected singlet δ_B (160 MHz; BF_3:OEt_2) P.N.D = 53.4 ppm, s)].

4.2.6 Synthesis of 4,7-dichloro-1,3,2-dithiaborolane (14)



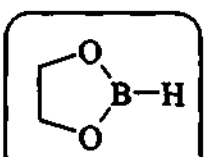
14

3,6-Dichloro-1,2-benzenedithiol (13) (107 mg, 0.51 mmol) was stirred in CH_2Cl_2 (5 ml) in a flame-dried two necked round-bottomed flask fitted with a reflux condenser and a rubber septum fitted over the second neck. To this solution was added drop wise borane-dimethyl sulfide complex (0.51 ml, 0.51 mmol) and the resulting solution was boiled

under reflux (40 °C) for 7 hours under an inert atmosphere of dry nitrogen to afford 4,7-dichloro-benzo-1,3,2-dithiaborolane (**14**) as a light yellow solution (100%), δ_B (160 MHz; BF_3:OEt_2) = 53.2 ppm, d, J_{B-H} = 149.9 Hz.

4.3 Synthesis of Oxygen-Containing Boranes

4.3.1 Synthesis of 1,3,2-dioxaborolane (16)

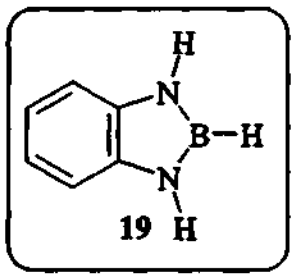


16

Borane-dimethyl-sulfide complex in CH_2Cl_2 (1.0 M, 5.0 ml, 5.0 mmol) was placed in a two necked, round-bottomed flask (25 ml) and cooled to -84 °C in a liquid nitrogen/ethyl acetate slurry. 1,2-Ethanediol (**15**) (0.28 ml, 5.0 mmol) in CH_2Cl_2 (5 ml) was added drop-wise over a period of 15 minutes through a nitrogen purged syringe. The resulting solution was allowed to warm to room temperature and maintained at this temperature for a further 20 hours to afford a mixture of 1,3,2-dioxaborolane (**16**) (15%) and 2,2'-(ethylenedioxy)bis-(1,3,2-dioxaborolane) (**17**) (70%). 1,3,2-dioxaborolane (**16**) δ_B (160 MHz; BF_3:OEt_2) = 28.4 ppm, d, J_{B-H} = 177.4 Hz; 2,2'- (ethylenedioxy)bis-(1,3,2-dioxaborolane) (**17**) δ_B (160 MHz; BF_3:OEt_2) = 22.9 ppm, s.

4.4 Preparation of Nitrogen-Containing Boranes

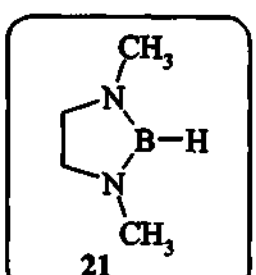
4.4.1 Synthesis of benzo-1,3,2-diazaborolane (19)



19

1,2-Diaminobenzene (**18**) (541 mg, 5.0 mmol) was dissolved in CH_2Cl_2 in a flame-dried round-bottomed flask. After complete dissolution of the solid 1,2-diaminobenzene, borane-dimethyl sulfide complex (1 M, 5.0 ml, 5.0 mmol) was introduced drop wise through the septum. The resulting mixture was stirred under reflux for 4 hours under a dry atmosphere of nitrogen, benzo-1,3,2-diazaborolane (**19**) was obtained as a clear liquid (95%) δ_B (160 MHz; BF_3:OEt_2) = 23.9 ppm, d, $J_{B\text{-}H}$ = 153.2 Hz.

4.4.2 Synthesis of 1,3-dimethyl-1,3,2-diazaborolane (21)



21

N,N'-diemethylethane-1,2-diamine (**20**) (1.21 ml, 11.3 mmol) and sodium borohydride (429 mg, 11.3 mmol) were mixed in dry THF (8 ml) in a dry, nitrogen flushed two necked round-bottomed flask. A solution of iodine (1.44g, 5.67 mmol) in THF (8 ml) was slowly added while stirring the contents of the flask. Rapid evolution of H_2 gas was

noted upon addition of the iodine solution, on completion of iodine addition, the resulting solution was refluxed for 14 hours. The reaction mixture was subsequently cooled to room temperature, following which sodium iodide precipitated out from the solution. The clear liquid was then drawn from this flask by a nitrogen-flushed syringe and was filtered through a 0.45 Nylon Cameo filter fitted between the needle and the syringe. 1,3-dimethyl-1,3,2-diazaborolane (**21**) was obtained as a clear liquid (80%) δ_B (160 MHz; BF_3:OEt_2) = 29.2 ppm, d, $J_{B\text{-}H}$ = 140.6 Hz.[r]

4.5 Hydroboration studies

4.5.1 Concentration Dependence study

For both 1,3,2-dithiaborolane (**7**) and 1,3,2-dithiaborinane (**9**), the following standard procedure for conducting concentration dependence studies for hydroboration of 1-octene were employed.[s]

To an oven dried, nitrogen purged quartz NMR tube 1,3,2-dithiaborolane (0.40 ml, 0.16 M), was added *via* syringe. The sample was analyzed to verify that no degradation of the compound had taken place prior to addition of the other reagents. 1-Octene in CH_2Cl_2 (0.40 ml, 10× [1,3,2-dithiaborolane] = 1.6 M) was then added to the to the NMR tube. The tube was then agitated prior to analysis. The time delay taken from injection of the 1-octene to the first scan in the spectrometer was measured by a stopwatch (time delay ranged between 35 to 40 seconds), the time delay was used to accurately measure the time interval between each data set in the NMR spectrometer. The spectrometer program was set to scan the contents of the tube initially very regularly and with time at slower intervals. Initially scans were recorded after every 5 min for the first 50 min, then after every 10 min for a subsequent 100 min, then after every 15 min for 75 min, then every 30

[r] The obtained NMR data are consistent with those reported in literature for this class of compounds.[71]

[s] The concentrations of the hydroborating agent and 1-octene were halved on mixing of the two reagents in the tube, therefore the concentration values shown below were halved upon mixing in the NMR tube.

min for 150 min and finally every 1 hour for a further 5 hours, 120 transients were used for each acquisition set which in turn represented a single data point..

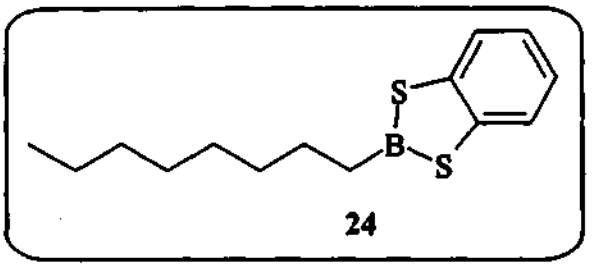
The concentrations of 1-octene were increased from 10 fold to 25 fold that of the hydroborating agent and the above method was repeated for each concentration. The data obtained was fitted using Microcal™ Origin™ 5.0 software. The raw data for each concentration dependence experiment is included in appendix A.

4.5.2 Temperature Dependence study

In order to determine $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values for the hydroboration of 1-octene with 1,3,2-dithiaborolane (7) or with 1,3,2-dithiaborinane (9), the following typical procedure was employed.

1,3,2-dithiaborolane (0.40 ml, 0.16 M) in CH_2Cl_2 was injected into an oven dried, nitrogen purged quartz NMR tube, 1-octene (0.40 ml, 15× [1,3,2-dithiaborolane] = 2.4 M) was then added to this solution. The resulting mixture was shaken vigorously, vented and placed in the NMR probe for analysis. Time delay measurements and acquisition time intervals were done in the same manner as discussed in the preceding section. Hydroboration experiments were conducted at 20 to 35 °C increasing in steps of 5 °C. For each experiment, the concentrations of the hydroborating agent and the olefin were kept constant. The data acquired was fitted with Microcal™ Origin™ 5.0 software to yield the activation parameters for each compound towards 1-octene. The raw data for each temperature dependence experiment is included in appendix B.

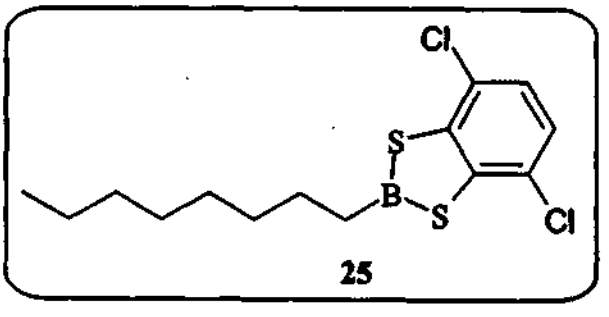
4.5.3 Hydroboration of 1-octene with benzo-1,3,2-dithiaborolane (24)



24

Benzo-1,3,2-dithiaborolane (**12**) (25.3 mg, 0.165 mmol) in diglyme (0.4 ml) was mixed with 1-octene (0.26 ml, 1.65 mmol) in a dry nitrogen flushed NMR tube, capped with a rubber septum and sealed with a parafilm. The tube was then inserted in an aluminium heating block, which was immersed in a silicon oil bath set to 150 °C. The contents of the tube were heated under reflux; the pressure build up in the tube was vented with a nitrogen purged syringe in every 20 min for 3 hours. This afforded a clear liquid of octyl-benzo-1,3,2-dithiaborolane (**24**) (65%), δ_B (160 MHz; BF_3:OEt_2) = 59.6 ppm, s.

4.5.4 Hydroboration of 1-octene with 4,7-dichloro-benzo-1,3,2-dithiaborolane (25)



25

4,7-Dichloro-benzo-1,3,2-dithiaborolane (**14**) (14.8 mg, 0.067 mmol) in CH_2Cl_2 (0.40 ml) was allowed to mix with 1-octene (0.11 ml, 0.67 mmol) in a dry NMR tube, and the hydroboration procedure as described above for benzo-1,3,2-dithiaborolane (**12**), to

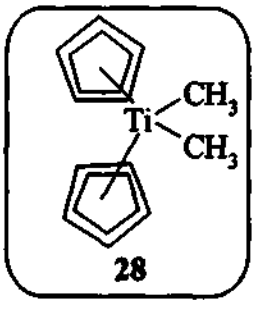
afford octyl-4,7-dichloro-benzo-1,3,2-dithiaborolane (**25**) (66%), δ_B (160 MHz; BF_3:OEt_2) = 58.5 ppm, s.

4.5.5 Attempted hydroboration of 1-octene with benzo-1,3,2-diazaborolane

Benzo-1,3,2-diazaborolane (**19**) (23.6 mg, 0.20 mmol) in diglyme (0.4 ml) and 1-octene (0.31 ml, 2.0 mmol) were allowed to mix in an NMR tube with a rubber septum, the resulting mixture was heated under reflux at 100 °C in a aluminium heating block for 10 days. Over this period there was no observable formation of octyl-benzo-1,3,2-diazaborolane (**26**) and the starting material benzo-1,3,2-diazaborolane (**19**) was recovered.

4.6 Titanium Catalyzed Hydroboration Reactions

4.6.1 Synthesis of bis(cyclopentadienyl) titanium dimethyl ($Cp_2Ti(CH_3)_2$) (28)



28

To a flame-dried two necked round-bottomed flask was placed bis(cyclopentadienyl) titanium dichloride (**27**) (249 mg, 1.0 mmol). The brick red solid (**27**) was dissolved in THF (10 ml), and the solution was cooled to 0 °C in an ice bath, following which methyllithium (2.0 ml, 2.0 mmol) in dry THF was added dropwise whilst stirring. The resulting mixture was shielded from light and stirred for 20 min.[127] Unreacted methyllithium was decomposed by addition of ice/water. The ether layer was separated

from the aqueous layer, and the solvent was removed *in vacuo*. An orange powder of bis(cyclopentadienyl) titanium dimethyl (**28**) was obtained after recrystallisation from n-pentane and stored in the dark (tin foil cover) at -10 °C in the freezer.

4.6.2 Cp_2TiMe_2 Catalyzed addition of benzo-1,3,2-dithiaborolane to 1-octene

To a dry, nitrogen filled round-bottomed flask was placed 1-octene (0.55 ml, 3.50 mmol), bis(cyclopentadienyl) titanium dimethyl (**28**) (29.1 mg, 0.140 mmol) and the solvent CH_2Cl_2 (5 ml). The resulting reaction mixture was stirred for 5 min, and benzo-1,3,2-dithiaborolane (**12**) (535 mg, 3.50 mmol) was injected slowly into the flask while stirring the contents of the flask. Surprisingly, no octylboronate ester was produced after 24 hour at 25 °C after inspection by NMR spectroscopy.

4.6.3 Cp_2TiMe_2 Catalyzed addition of benzo-1,3,2-diazaborolane to 1-octene

Benzo-1,3,2-diazaborolane (**19**) (591 mg, 5.0 mmol), 1-octene (0.78 ml, 5.0 mmol) and bis(cyclopentadienyl) titanium dimethyl (**28**) (41.6 mg, 0.20 mmol) were added to a dry, nitrogen filled round-bottomed flask. The contents of the flask were dissolved in CH_2Cl_2 (5 ml), and stirred for 5 minutes. This reaction afforded no octylboronate ester after 24 hour at 25 °C.

4.7 Tris-(triphenylphosphine)-rhodium (I)-chloride ($Rh(PPh_3)_3Cl$) catalyzed hydroboration reactions

The hydroborating agent was injected into an oven dried, nitrogen purged and septum capped quartz NMR tube. The hydroborating agent under investigation was analyzed prior to the addition of the other reagents in order to confirm its purity. To this solution was added simultaneously the olefin and Tris-(triphenylphosphine)-rhodium (I)-chloride

(2 mol%) which was dissolved in CH_2Cl_2 (0.5 ml) in a separate vial. The contents of the tube were shaken vigorously and the tube was inserted into the NMR spectrometer. The contents of the tube were subsequently analyzed in every 2 hours for 24 hours to monitor the progress of formation of the target alkylboronate ester.

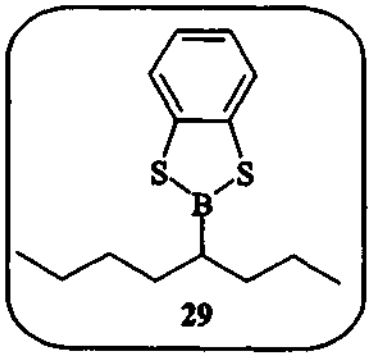
The amounts for each reactant used and yields of alkylboronate esters produced for each experiment are given in the following sections.

4.7.1 $RhCl(PPh_3)_3$ catalyzed addition of benzo-1,3,2-dithiaborolane to 1-octene (24)

Benzo-1,3,2-dithiaborolane (12)	0.40 ml, 0.248 mmol
1-Octene	0.39 ml, 2.48 mmol
$RhCl(PPh_3)_3$	46.3 mg, 0.050 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours

Afforded octyl-benzo-1,3,2-dithiaborolane (24) (60%), δ_B (160 MHz; $BF_3{:}OEt_2$) = 59.6 ppm, s.

4.7.2 $RhCl(PPh_3)_3$ catalyzed addition of benzo-1,3,2-dithiaborolane to 4-octene (29)



29

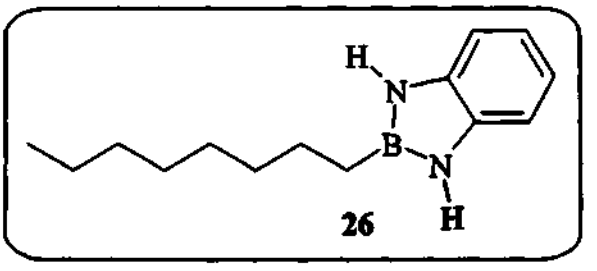
Benzo-1,3,2-dithiaborolane (12)	0.40 ml, 0.248 mmol
Trans-4-octene	0.39 ml, 2.48 mmol
$RhCl(PPh_3)_3$	46.3 mg, 0.050 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours

The reaction afforded 2-(pentyl-1-propyl)-benzo-1,3,2-dithiaborolane (29) (59%), δ_B (160 MHz; BF_3:OEt_2) = 59.8 ppm, s. This product was subsequently oxidized by addition of NaOH (0.83 ml, 3 M) and H_2O_2 (0.02 ml of 50% v/v) solution to afford 4-octanol δ_H(500 MHz; $CDCl_3$) 0.95 (3H, t, 2 ($C\underline{H}_3$-)), 1.41 (2H, m, 2 ($CH_3C\underline{H}_2$-)), 1.32 (2H, m, $CH_3CH_2C\underline{H}_2CHOHCH_2$-), 4.71 (1H, s, -$CH_2CHO\underline{H}CH_2$-), 3.61 (1H, m, -$CH_2C\underline{H}OHCH_2$-), 1.49 (2H, m, $CH_3CH_2CH_2CHOHC\underline{H}_2$-) 1.39 (2H, m, $CH_3CH_2CH_2CHOHCH_2C\underline{H}_2$-); *m/z* 130 ($M^+$, 20%), 87 (100) 73 (52), 69 (36) and 55 (66).

4.7.3 $RhCl(PPh_3)_3$ catalyzed addition of 4,7-dichloro-1,3,2-benzodithiaborolane to 1- and 4-octene

4,7-Dichloro-1,3,2-benzodithiaborolane (14)	0.40 ml, 0.067 mmol
1-Octene or *Trans*-4-octene	0.10 ml, 0.67 mmol
$RhCl(PPh_3)_3$	13.3 mg, 0.013 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours
Octyl-4,7-dichloro-1,3,2-benzodithiaborolane	no reaction

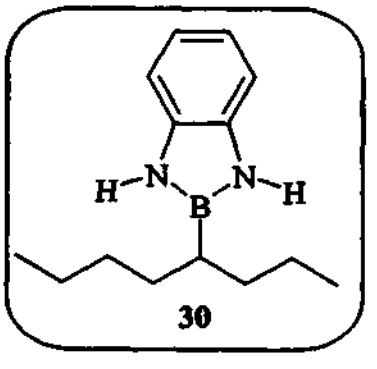
4.7.4 $RhCl(PPh_3)_3$ catalyzed addition of benzo-1,3,2-diazaborolane to 1-octene (26)



26

Benzo-1,3,2-diazaborolane (19)	0.40 ml, 0.20 mmol
1-Octene	0.31 ml, 2.0 mmol
$RhCl(PPh_3)_3$	37.0 mg, 0.040 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours
Octyl-benzo-1,3,2-diazaborolane (26)	70%, δ_B (160 MHz; $BF_3{:}OEt_2$) = 31.6 ppm, s.

4.7.5 $RhCl(PPh_3)_3$ catalyzed addition of benzo-1,3,2-diazaborolane to 4-octene (30)



30

Benzo-1,3,2-diazaborolane (19)	0.40 ml, 0.20 mmol
trans-4-Octene	0.31 ml, 2.0 mmol
$RhCl(PPh_3)_3$	37.0 mg, 0.040 mmol

CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours

^{11}B NMR analysis showed no alkylboronate ester formation even at boiling CH_2Cl_2 for 30 hours.

4.7.6 $RhCl(PPh_3)_3$ catalyzed addition of 1,3-dimethyl-1,3,2-diazaborolane to 1-and 4-octene

1,3-Dimethyl-1,3,2-diazaborolane (**21**)	0.40 ml, 0.46 mmol
1-Octene or *trans*-4-Octene	0.72 ml, 4.60 mmol
$RhCl(PPh_3)_3$	85.1 mg, 0.092 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C or 40 °C
Reaction time	30 hours

No reaction was observed with either 1-octene or 4-octene.

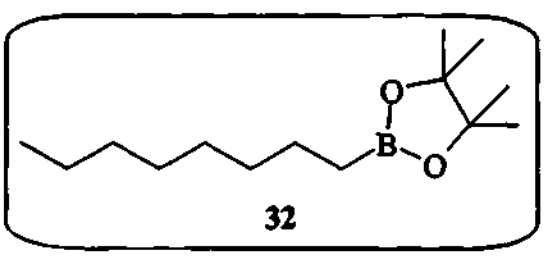
4.7.7 $RhCl(PPh_3)_3$ catalyzed addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to *trans*-4-octene

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (pinacolborane) used in the following experiments was purchased from Sigma-Aldrich. The pinacolborane was shown by NMR spectroscopy to contain a significant percentage of the disproportionated product (*ca.* 40%). As this species played no part in the reactions it could be discounted, however, the percentage of pinacolborane in each sample was determined by integration of the ^{11} B NMR spectra acquired prior to addition of the catalyst and the olefin.

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane	0.40 ml (58%)[θ], 0.23 mmol
Trans-4-octene	0.36 ml, 2.32 mmol
$RhCl(PPh_3)_3$	42.9 mg, 0.046 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours

On completion this reaction showed no product formation.

4.7.8 $RhCl(PPh_3)_3$ catalyzed addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane to 1-octene (32)



32

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane	0.40 ml (47%), 0.19 mmol
1-Octene	0.30 ml, 1.88 mmol
$RhCl(PPh_3)_3$	34.9 mg, 0.038 mmol
CH_2Cl_2	0.50 ml
Reaction temperature	25 °C
Reaction time	24 hours

The reaction afforded octyl-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (32) in 79% yield, δ_B (160 MHz; $BF_3{:}OEt_2$) = 34.4 ppm, s.

[θ] The bracketed percentage represents the amount of pinacolborane contained in the stock solution prior addition of the alkene and the catalyst. This was determined by integration of the ^{11}B NMR spectrum of the stock solution.

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Appendix

6. APPENDIX

6.1 Appendix A

6.1.1 Hydroboration of 1-octene with 1,3,2-Dithiaborolane (7)(Concentration Dependence Study at 25 °C)

Table 6.1 Original data for hydroboration of 10× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	73	0.158	0.000
60	92	1	72	0.156	0.002
480	512	6	62	0.134	0.013
900	932	11	57	0.123	0.024
1320	1352	14	52	0.112	0.030
1740	1772	16	47	0.102	0.035
2160	2192	18	43	0.093	0.039
2580	2612	20	41	0.089	0.043
3000	3032	21	38	0.082	0.045
3420	3452	23	36	0.078	0.050
3840	3872	24	34	0.073	0.052
4260	4292	25	32	0.069	0.054
4980	5012	26	29	0.063	0.056
5700	5732	27	27	0.058	0.058
6420	6452	28	25	0.054	0.061
7140	7172	29	24	0.052	0.063
7860	7892	30	22	0.048	0.065
8580	8612	31	21	0.045	0.067
9300	9332	31	20	0.043	0.067
10020	10052	32	19	0.041	0.069
10740	10772	32	18	0.039	0.069
11460	11492	33	17	0.037	0.071
12480	12512	33	16	0.035	0.071
13500	13532	34	15	0.032	0.073
14520	14552	34	15	0.032	0.073
15540	15572	35	14	0.030	0.076
16560	16592	35	13	0.028	0.076
18480	18512	35	12	0.026	0.076
20400	20432	36	12	0.026	0.078
22320	22352	36	11	0.024	0.078
24240	24272	37	10	0.022	0.080
27960	27992	37	9	0.019	0.080
31680	31712	38	8	0.017	0.082

Table 6.2 Original data for hydroboration of 15× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	67	0.161	0.000
60	107	2	67	0.161	0.005
480	527	7	56	0.134	0.017
900	947	10	47	0.113	0.024
1320	1367	13	41	0.098	0.031
1740	1787	15	37	0.089	0.036
2160	2207	16	33	0.079	0.038
2580	2627	18	31	0.074	0.043
3000	3047	19	28	0.067	0.046
3420	3467	20	26	0.062	0.048
3840	3887	20	24	0.058	0.048
4260	4307	21	23	0.055	0.050
4980	5027	22	21	0.050	0.053
5700	5747	23	19	0.046	0.055
6420	6467	23	18	0.043	0.055
7140	7187	24	16	0.038	0.058
7860	7907	24	15	0.036	0.058
8580	8627	25	14	0.034	0.060
9300	9347	25	13	0.031	0.060
10020	10067	26	13	0.031	0.062
10740	10787	26	12	0.029	0.062
11460	11507	26	12	0.029	0.062
12480	12527	26	11	0.026	0.062
13500	13547	27	10	0.024	0.065
14520	14567	27	10	0.024	0.065
15540	15587	27	9	0.022	0.065
16560	16607	27	9	0.022	0.065
18480	18527	28	8	0.019	0.067
20400	20447	28	7	0.017	0.067
22320	22367	28	7	0.017	0.067
24240	24287	28	6	0.014	0.067
27960	28007	29	5	0.012	0.070
31680	31727	29	5	0.012	0.070
35400	35447	29	5	0.012	0.070
39120	39167	29	4	0.010	0.070
42840	42887	29	4	0.010	0.070

Table 6.3 Original data for hydroboration of 20×[1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	67	0.131	0.000
60	104	2	65	0.127	0.004
480	524	8	52	0.101	0.016
900	944	12	44	0.086	0.023
1320	1364	14	38	0.074	0.027
1740	1784	16	34	0.066	0.031
2160	2204	18	30	0.059	0.035
2580	2624	19	28	0.055	0.037
3000	3044	20	26	0.051	0.039
3420	3464	21	24	0.047	0.041
3840	3884	22	22	0.043	0.043
4260	4304	22	21	0.041	0.043
4980	5024	23	19	0.037	0.045
5700	5744	24	17	0.033	0.047
6420	6464	25	16	0.031	0.049
7140	7184	25	15	0.029	0.049
7860	7904	26	14	0.027	0.051
8580	8624	26	13	0.025	0.051
9300	9344	26	12	0.023	0.051
10020	10064	27	12	0.023	0.053
10740	10784	27	11	0.021	0.053
11460	11504	27	10	0.020	0.053
12480	12524	28	10	0.020	0.055
13500	13544	28	9	0.018	0.055
14520	14564	28	9	0.018	0.055
15540	15584	28	8	0.016	0.055
16560	16604	28	8	0.016	0.055
18480	18524	29	7	0.014	0.057
20400	20444	29	7	0.014	0.057
22320	22364	29	6	0.012	0.057
24240	24284	29	6	0.012	0.057
26160	26204	30	3	0.006	0.059
29880	29924	30	3	0.006	0.059
33600	33644	30	3	0.006	0.059
37320	37364	30	3	0.006	0.059
41040	41084	31	3	0.006	0.060

Table 6.4 Original data for hydroboration of 25× [1-octene] with 1,3,2-dithiaborolane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	57	0.123	0.000
60	103	1	56	0.120	0.002
480	523	6	44	0.095	0.013
900	943	7	37	0.080	0.015
1320	1363	11	32	0.069	0.024
1740	1783	12	28	0.060	0.026
2160	2203	13	25	0.054	0.028
2580	2623	14	23	0.049	0.030
3000	3043	15	21	0.045	0.032
3420	3463	15	19	0.041	0.032
3840	3883	16	18	0.039	0.034
4260	4303	16	17	0.037	0.034
4980	5023	17	15	0.032	0.037
5700	5743	17	14	0.030	0.037
6420	6463	18	13	0.028	0.039
7140	7183	18	12	0.026	0.039
7860	7903	19	11	0.024	0.041
8580	8623	19	10	0.022	0.041
9300	9343	19	10	0.022	0.041
10020	10063	19	9	0.019	0.041
10740	10783	20	9	0.019	0.043
11460	11503	20	8	0.017	0.043
12480	12523	20	8	0.017	0.043
13500	13543	20	7	0.015	0.043
14520	14563	20	7	0.015	0.043
15540	15583	20	7	0.015	0.043
16560	16603	20	6	0.013	0.043
18480	18523	21	6	0.013	0.045
20400	20443	21	5	0.011	0.045
22320	22363	21	5	0.011	0.045
24240	24283	21	5	0.011	0.045
27960	28003	21	4	0.009	0.045
31680	31723	21	4	0.009	0.045
35400	35443	21	3	0.006	0.045
39120	39163	22	3	0.006	0.047
42840	42883	22	3	0.006	0.047

6.1.2 Hydroboration of 1-octene with 1,3,2-Dithiaborinane (9)(Concentration Dependence Study at 25 °C)

Table 6.5 Original data for hydroboration of 10× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	38	0.156	0.000
60	113	1	38	0.156	0.004
480	533	2	37	0.151	0.008
900	953	3	33	0.135	0.012
1320	1373	4	30	0.123	0.016
1740	1793	5	28	0.115	0.020
2160	2213	5	26	0.106	0.020
2580	2633	6	24	0.098	0.025
3000	3053	6	23	0.094	0.025
3420	3473	6	21	0.086	0.025
3840	3893	7	20	0.082	0.029
4260	4313	7	19	0.078	0.029
4980	5033	7	18	0.074	0.029
5700	5753	8	17	0.070	0.033
6420	6473	8	15	0.061	0.033
7140	7193	8	15	0.061	0.033
7860	7913	9	14	0.057	0.037
8580	8633	9	13	0.053	0.037
9300	9353	9	13	0.053	0.037
10020	10073	9	12	0.049	0.037
10740	10793	9	12	0.049	0.037
11460	11513	9	12	0.049	0.037
12480	12533	10	11	0.045	0.041
13500	13553	10	12	0.049	0.041
14520	14573	10	11	0.045	0.041
15540	15593	11	11	0.045	0.045
16560	16613	11	10	0.041	0.045
18480	18533	11	10	0.041	0.045
20400	20453	11	10	0.041	0.045
22320	22373	12	10	0.041	0.049
24240	24293	12	10	0.041	0.049
26160	26213	12	10	0.041	0.049
28080	28133	13	10	0.041	0.053
31800	31853	14	10	0.041	0.057
35520	35573	14	10	0.041	0.057

Table 6.6 Original data for hydroboration of 15× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	46	0.130	0.000
60	100	1	43	0.121	0.003
480	520	2	38	0.107	0.006
900	940	3	34	0.096	0.008
1320	1360	3	31	0.087	0.008
1740	1780	4	29	0.082	0.011
2160	2200	4	27	0.076	0.011
2580	2620	5	23	0.065	0.014
3000	3040	5	23	0.065	0.014
3420	3460	6	22	0.062	0.017
3840	3880	6	21	0.059	0.017
4260	4300	6	19	0.054	0.017
4980	5020	7	18	0.051	0.020
5700	5740	7	17	0.048	0.020
6420	6460	7	17	0.048	0.020
7140	7180	8	16	0.045	0.023
7860	7900	8	15	0.042	0.023
8580	8620	8	14	0.039	0.023
9300	9340	8	14	0.039	0.023
10020	10060	8	13	0.037	0.023
10740	10780	9	13	0.037	0.025
11460	11500	9	12	0.034	0.025
12480	12520	9	12	0.034	0.025
13500	13540	9	12	0.034	0.025
14520	14560	9	12	0.034	0.025
15540	15580	9	11	0.031	0.025
16560	16600	10	11	0.031	0.028
18480	18520	11	11	0.031	0.031
20400	20440	11	11	0.031	0.031
22320	22360	11	11	0.031	0.031
24240	24280	12	10	0.028	0.034
26160	26200	12	10	0.028	0.034
28080	28120	13	10	0.028	0.037
31800	31840	13	10	0.028	0.037
35520	35560	14	10	0.028	0.039
39240	39280	15	10	0.028	0.042
42960	43000	15	10	0.028	0.042
46680	46720	16	10	0.028	0.045
50400	50440	17	10	0.028	0.048

Table 6.7 Original data for hydroboration of 20× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	41	0.137	0.000
60	100	1	41	0.137	0.003
480	520	2	34	0.114	0.007
900	940	3	31	0.104	0.010
1320	1360	4	28	0.094	0.013
1740	1780	4	25	0.084	0.013
2160	2200	5	23	0.077	0.017
2580	2620	5	22	0.074	0.017
3000	3040	5	21	0.070	0.017
3420	3460	6	19	0.064	0.020
3840	3880	6	18	0.060	0.020
4260	4300	6	18	0.060	0.020
4980	5020	7	16	0.054	0.023
5700	5740	7	15	0.050	0.023
6420	6460	8	14	0.047	0.027
7140	7180	8	13	0.044	0.027
7860	7900	8	13	0.044	0.027
8580	8620	8	12	0.040	0.027
9300	9340	9	12	0.040	0.030
10020	10060	9	11	0.037	0.030
10740	10780	9	11	0.037	0.030
11460	11500	10	11	0.037	0.033
12480	12520	10	10	0.033	0.033
13500	13540	10	10	0.033	0.033
14520	14560	11	10	0.033	0.037

Table 6.8 Original data for hydroboration of 25× [1-octene] with 1,3,2-dithiaborinane.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	31	0.108	0.000
60	100	1	36	0.108	0.003
480	520	2	31	0.093	0.006
900	940	3	27	0.081	0.009
1320	1360	4	24	0.072	0.012
1740	1780	4	22	0.066	0.012
2160	2200	5	20	0.060	0.015
2580	2620	5	19	0.057	0.015
3000	3040	5	18	0.054	0.015
3420	3460	6	17	0.051	0.018
3840	3880	6	16	0.048	0.018
4260	4300	6	15	0.045	0.018
4980	5020	7	14	0.042	0.021
5700	5740	7	13	0.039	0.021
6420	6460	7	12	0.036	0.021
7140	7180	8	11	0.033	0.024
7860	7900	8	11	0.033	0.024
8580	8620	8	10	0.030	0.024
9300	9340	9	10	0.030	0.027
10020	10060	9	9	0.027	0.027
10740	10780	9	9	0.027	0.027
11460	11500	9	9	0.027	0.027
12480	12520	9	8	0.024	0.027
13500	13540	10	8	0.024	0.030
14520	14560	10	8	0.024	0.030
15540	15580	11	8	0.024	0.033
16560	16600	11	7	0.021	0.033
18480	18520	11	7	0.021	0.033
20400	20440	12	7	0.021	0.036

6.2 Appendix B

6.2.1 Hydroboration of 15× [1-octene] with 1,3,2-Dithiaborolane (7) (Temperature Dependence Study)

Table 6.9 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane at 20°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	53	0.124	0.000
60	398	3	51	0.119	0.007
480	818	5	51	0.119	0.012
900	1238	7	47	0.110	0.016
1320	1658	8	43	0.100	0.019
1740	2078	10	40	0.093	0.023
2160	2498	11	38	0.089	0.026
2580	2918	11	35	0.082	0.026
3000	3338	12	33	0.077	0.028
3420	3758	13	32	0.075	0.030
3840	4178	14	30	0.070	0.033
4260	4598	14	28	0.065	0.033
4980	5318	15	27	0.063	0.035
5700	6038	16	25	0.058	0.037
6420	6758	16	23	0.054	0.037
7140	7478	17	22	0.051	0.040
7860	8198	17	21	0.049	0.040
8580	8918	18	19	0.044	0.042
9300	9638	18	19	0.044	0.042
10020	10358	18	18	0.042	0.042
10740	11078	19	17	0.040	0.044
11460	11798	19	16	0.037	0.044
12480	12818	19	15	0.035	0.044
13500	13838	20	15	0.035	0.047
14520	14858	20	14	0.033	0.047
15540	15878	20	13	0.030	0.047
16560	16898	21	13	0.030	0.049
18480	18818	21	12	0.028	0.049
20400	20738	21	11	0.026	0.049
22320	22658	21	10	0.023	0.049
24240	24578	22	10	0.023	0.051
26160	26498	22	9	0.021	0.051
28080	28418	22	8	0.019	0.051
31800	32138	22	8	0.019	0.051

Table 6.10 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 25°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	67	0.161	0.000
60	107	2	67	0.161	0.005
480	527	7	56	0.134	0.017
900	947	10	47	0.113	0.024
1320	1367	13	41	0.098	0.031
1740	1787	15	37	0.089	0.036
2160	2207	16	33	0.079	0.038
2580	2627	18	31	0.074	0.043
3000	3047	19	28	0.067	0.046
3420	3467	20	26	0.062	0.048
3840	3887	20	24	0.058	0.048
4260	4307	21	23	0.055	0.050
4980	5027	22	21	0.050	0.053
5700	5747	23	19	0.046	0.055
6420	6467	23	18	0.043	0.055
7140	7187	24	16	0.038	0.058
7860	7907	24	15	0.036	0.058
8580	8627	25	14	0.034	0.060
9300	9347	25	13	0.031	0.060
10020	10067	26	13	0.031	0.062
10740	10787	26	12	0.029	0.062
11460	11507	26	12	0.029	0.062
12480	12527	26	11	0.026	0.062
13500	13547	27	10	0.024	0.065
14520	14567	27	10	0.024	0.065
15540	15587	27	9	0.022	0.065
16560	16607	27	9	0.022	0.065
18480	18527	28	8	0.019	0.067
20400	20447	28	7	0.017	0.067
22320	22367	28	7	0.017	0.067
24240	24287	28	6	0.014	0.067
27960	28007	29	5	0.012	0.070
31680	31727	29	5	0.012	0.070
35400	35447	29	5	0.012	0.070
39120	39167	29	4	0.010	0.070
42840	42887	29	4	0.010	0.070

Table 6.11 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 30°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	62	0.142	0.000
60	102	4	59	0.135	0.009
480	522	11	51	0.117	0.025
900	942	15	43	0.099	0.034
1320	1362	18	38	0.087	0.041
1740	1782	19	34	0.078	0.044
2160	2202	21	31	0.071	0.048
2580	2622	22	29	0.066	0.050
3000	3042	23	27	0.062	0.053
3420	3462	24	25	0.057	0.055
3840	3882	25	24	0.055	0.057
4260	4302	25	23	0.053	0.057
4980	5022	27	20	0.046	0.062
5700	5742	27	19	0.044	0.062
6420	6462	28	18	0.041	0.064
7140	7182	28	17	0.039	0.064
7860	7902	29	15	0.034	0.066
8580	8622	29	15	0.034	0.066
9300	9342	30	14	0.032	0.069
10020	10062	30	13	0.030	0.069
10740	10782	30	13	0.030	0.069
11460	11502	31	12	0.027	0.071
12480	12522	31	12	0.027	0.071
13500	13542	32	11	0.025	0.073
14520	14562	31	11	0.025	0.071
15540	15582	32	10	0.023	0.073
16560	16602	32	9	0.021	0.073
18480	18522	33	9	0.021	0.076
20400	20442	33	8	0.018	0.076
22320	22362	33	8	0.018	0.076
24240	24282	33	7	0.016	0.076
26160	26202	33	7	0.016	0.076
28080	28122	34	7	0.016	0.078
31800	31842	34	6	0.014	0.078
35520	35562	34	6	0.014	0.078
39240	39282	35	5	0.011	0.080
42960	43002	35	5	0.011	0.080
46680	46722	35	5	0.011	0.080
50400	50442	34	4	0.009	0.078

Table 6.12 Original data for hydroboration of 1-octene with 1,3,2-dithiaborolane at 35°C.

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	product conc. (M)
0	0	0	56	0.118	0.000
60	95	4	56	0.118	0.008
480	515	13	37	0.078	0.027
900	935	17	28	0.059	0.036
1320	1355	20	23	0.048	0.042
1740	1775	22	20	0.042	0.046
2160	2195	23	18	0.038	0.048
2580	2615	23	16	0.034	0.048
3000	3035	24	15	0.031	0.050
3420	3455	25	13	0.027	0.052
3840	3875	25	12	0.025	0.052
4260	4295	25	12	0.025	0.052
4980	5015	26	11	0.023	0.055
5700	5735	27	10	0.021	0.057
6420	6455	27	9	0.019	0.057
7140	7175	27	8	0.017	0.057
7860	7895	27	8	0.017	0.057
8580	8615	28	7	0.015	0.059
9300	9335	28	7	0.015	0.059
10020	10055	28	7	0.015	0.059
10740	10775	28	7	0.015	0.059
11460	11495	28	6	0.013	0.059
12480	12515	28	6	0.013	0.059
13500	13535	29	6	0.013	0.061
14520	14555	29	6	0.013	0.061
15540	15575	29	5	0.010	0.061
16560	16595	29	5	0.010	0.061
18480	18515	29	5	0.010	0.061
20400	20435	29	4	0.008	0.061
22320	22355	29	4	0.008	0.061
24240	24275	29	4	0.008	0.061
26160	26195	29	4	0.008	0.061
28080	28115	29	4	0.008	0.061

6.2.2 Hydroboration of 15× [1-octene] with 1,3,2-Dithiaborinane (9)(Temperature Dependence Study)

Table 6.13 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane at 20°C

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	45	0.162	0.000
60	101	1	44	0.158	0.004
480	521	2	40	0.144	0.007
900	941	2	36	0.130	0.007
1320	1361	3	34	0.122	0.011
1740	1781	3	32	0.115	0.011
2160	2201	4	30	0.108	0.014
2580	2621	4	29	0.104	0.014
3000	3041	4	27	0.097	0.014
3420	3461	5	26	0.094	0.018
3840	3881	5	25	0.090	0.018
4260	4301	5	24	0.086	0.018
4980	5021	5	23	0.083	0.018
5700	5741	6	22	0.079	0.022
6420	6461	6	20	0.072	0.022
7140	7181	6	19	0.068	0.022
7860	7901	7	18	0.065	0.025
8580	8621	7	17	0.061	0.025
9300	9341	7	16	0.058	0.025
10020	10061	7	16	0.058	0.025
10740	10781	8	15	0.054	0.029
11460	11501	8	14	0.050	0.029
12480	12521	8	14	0.050	0.029
13500	13541	8	13	0.047	0.029
14520	14561	8	12	0.043	0.029
15540	15581	9	12	0.043	0.032
16560	16601	9	12	0.043	0.032
18480	18521	9	11	0.040	0.032
20400	20441	10	10	0.036	0.036
22320	22361	10	10	0.036	0.036
24240	24281	10	10	0.036	0.036
26160	26201	11	9	0.032	0.040
28080	28121	11	9	0.032	0.040
31800	31841	12	9	0.032	0.043
35520	35561	12	8	0.029	0.043

Table 6.14 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 25°C

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	46	0.130	0.000
60	100	1	43	0.121	0.003
480	520	2	38	0.107	0.006
900	940	3	34	0.096	0.008
1320	1360	3	31	0.087	0.008
1740	1780	4	29	0.082	0.011
2160	2200	4	27	0.076	0.011
2580	2620	5	23	0.065	0.014
3000	3040	5	23	0.065	0.014
3420	3460	6	22	0.062	0.017
3840	3880	6	21	0.059	0.017
4260	4300	6	19	0.054	0.017
4980	5020	7	18	0.051	0.020
5700	5740	7	17	0.048	0.020
6420	6460	7	17	0.048	0.020
7140	7180	8	16	0.045	0.023
7860	7900	8	15	0.042	0.023
8580	8620	8	14	0.039	0.023
9300	9340	8	14	0.039	0.023
10020	10060	8	13	0.037	0.023
10740	10780	9	13	0.037	0.025
11460	11500	9	12	0.034	0.025
12480	12520	9	12	0.034	0.025
13500	13540	9	12	0.034	0.025
14520	14560	9	12	0.034	0.025
15540	15580	9	11	0.031	0.025
16560	16600	10	11	0.031	0.028
18480	18520	11	11	0.031	0.031
20400	20440	11	11	0.031	0.031
22320	22360	11	11	0.031	0.031
24240	24280	12	10	0.028	0.034
26160	26200	12	10	0.028	0.034
28080	28120	13	10	0.028	0.037
31800	31840	13	10	0.028	0.037
35520	35560	14	10	0.028	0.039
39240	39280	15	10	0.028	0.042
42960	43000	15	10	0.028	0.042
46680	46720	16	10	0.028	0.045
50400	50440	17	10	0.028	0.048

Table 6.15 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 30°C

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	41	0.142	0.000
60	102	1	44	0.142	0.003
480	522	2	38	0.123	0.006
900	942	3	32	0.103	0.010
1320	1362	4	30	0.097	0.013
1740	1782	4	27	0.087	0.013
2160	2202	5	25	0.081	0.016
2580	2622	5	24	0.078	0.016
3000	3042	6	22	0.071	0.019
3420	3462	6	21	0.068	0.019
3840	3882	6	20	0.065	0.019
4260	4302	7	19	0.061	0.023
4980	5022	7	18	0.058	0.023
5700	5742	8	17	0.055	0.026
6420	6462	8	16	0.052	0.026
7140	7182	8	15	0.048	0.026
7860	7902	9	14	0.045	0.029
8580	8622	9	14	0.045	0.029
9300	9342	9	13	0.042	0.029
10020	10062	10	13	0.042	0.032
10740	10782	10	13	0.042	0.032
11460	11502	10	12	0.039	0.032
12480	12522	11	12	0.039	0.036
13500	13542	11	12	0.039	0.036
14520	14562	11	11	0.036	0.036
15540	15582	12	11	0.036	0.039
16560	16602	12	11	0.036	0.039
18480	18522	13	11	0.036	0.042
20400	20442	14	11	0.036	0.045
22320	22362	14	10	0.032	0.045
24240	24282	15	10	0.032	0.048
26160	26202	16	10	0.032	0.052
28080	28122	16	10	0.032	0.052
31800	31842	18	10	0.032	0.058
35520	35562	19	10	0.032	0.061
39240	39282	21	10	0.032	0.068
42960	43002	22	10	0.032	0.071

Table 6.16 Original data for hydroboration of 1-octene with 1,3,2-dithiaborinane 35°C

Time (sec)	Corrected time (sec)	product (% integral)	reactant (% integral)	Reactant conc. (M)	Product conc. (M)
0	0	0	37	0.123	0.000
60	100	0	44	0.123	0.000
480	520	2	36	0.101	0.006
900	940	3	31	0.087	0.008
1320	1360	4	28	0.078	0.011
1740	1780	5	25	0.070	0.014
2160	2200	5	23	0.064	0.014
2580	2620	6	22	0.061	0.017
3000	3040	6	20	0.056	0.017
3420	3460	7	19	0.053	0.020
3840	3880	7	18	0.050	0.020
4260	4300	8	17	0.048	0.022
4980	5020	8	16	0.045	0.022
5700	5740	9	15	0.042	0.025
6420	6460	9	14	0.039	0.025
7140	7180	10	13	0.036	0.028
7860	7900	10	13	0.036	0.028
8580	8620	11	13	0.036	0.031
9300	9340	11	12	0.034	0.031
10020	10060	12	12	0.034	0.034
10740	10780	13	12	0.034	0.036
11460	11500	13	12	0.034	0.036
12480	12520	14	11	0.031	0.039
13500	13540	14	11	0.031	0.039
14520	14560	15	11	0.031	0.042
15540	15580	16	11	0.031	0.045
16560	16600	16	11	0.031	0.045
18480	18520	19	11	0.031	0.053
20400	20440	20	11	0.031	0.056

6.3 Appendix C

6.3.1 Spartan output log file from geometry optimization of 1,3,2-dioxaborolane (16)

```
Job WF11495 started on DIAMOND10 at Wed Dec 01 09:38:18
2004
Jaguar version 3.5, release  42

  Job name:                WF11495

  Task:                    Geometry optimization

  Stoichiometry:           BC2H5O2
  Molecular weight:        72.04 amu
  Molecular charge:           0
  Spin multiplicity:          1
  Point Group:             C1

  SCF method:              B3LYP
  Basis set:               LACV3P+**
  Basis functions:           140

  Total electrons:            38
  Alpha electrons:            19
  Beta electrons:             19
  Total orbitals:            145
  Core orbitals:              19
  Open-shell orbitals:         0
  Occupied orbitals:          19
  Shells:                      1

Non-default options chosen:
   SCF calculation type: DFT
   DFT=Becke_3_Parameter/HF+Slater+Becke88+VWN+LYP (B3LYP)
   Geometry will be optimized in redundant internal
coordinates
   Molecular symmetry not used
   Initial Hessian: from previous calculation

Iter      Energy        Gmax        Grms        Dmax        Drms
1  -254.675577 *   0.00039 *   0.00013 *   0.00155 *   0.00057
*

  ************************************************************
  **              Geometry optimization complete            **
  ************************************************************
```

```
          Final energy ..............  -254.67557715586

Job WF11495 completed on DIAMOND10 at Wed Dec 01 09:56:01
2004
  Reason for exit: Successful completion
  Titan Program CPU Time : 000:16:55.9
  Titan Program Wall Time: 000:17:44.0
```

6.3.2 Spartan output log file from geometry optimization of 1,3,2-dithiaborolane (7)

```
Job WF9471 started on DIAMOND10 at Tue Nov 30 08:22:48 2004
Jaguar version 3.5, release  42

  Job name:              WF9471

  Task:                  Geometry optimization

  Stoichiometry:         BC2H5S2
  Molecular weight:     103.99 amu
  Molecular charge:        0
  Spin multiplicity:       1
  Point Group:           C1

  SCF method:            B3LYP
  Basis set:             LACV3P+**
  Basis functions:         156

  Total electrons:         54
  Alpha electrons:         27
  Beta electrons:          27
  Total orbitals:         161
  Core orbitals:           27
  Open-shell orbitals:      0
  Occupied orbitals:       27
  Shells:                   1

Non-default options chosen:
   SCF calculation type: DFT
   DFT=Becke_3_Parameter/HF+Slater+Becke88+VWN+LYP (B3LYP)
   Geometry will be optimized in redundant internal
coordinates
   Molecular symmetry not used
   Initial Hessian: from previous calculation
```

```
Iter     Energy        Gmax        Grms        Dmax        Drms
1  -900.580880 *   0.03329 .   0.01339 .   0.12984 .   0.05483
2  -900.589751 .   0.00712 .   0.00307 .   0.05800 .   0.02262
3  -900.590592 .   0.00304 .   0.00134 .   0.02687 .   0.00934
.
4  -900.590681 .   0.00101 .   0.00033 .   0.16020 .   0.05477
5  -900.591108 .   0.00416 .   0.00161 .   0.15657 .   0.05486
  ** restarting optimization from step    5 **
5  -900.590188 .   0.00416 .   0.00161 .   0.16976 .   0.05476
7  -900.592259 .   0.00398 .   0.00138 .   0.16308 .   0.05479
8  -900.593521 .   0.00420 .   0.00151 .   0.14819 .   0.05477
9  -900.594282 .   0.00410 .   0.00207 .   0.16678 .   0.05488
** restarting optimization from step    9 **
9  -900.593088 .   0.00410 .   0.00207 .   0.01898 .   0.00994
11  -900.594394 .   0.00271 .   0.00108 .   0.05355 . .01923
.
  ** restarting optimization from step   11 **
   11  -900.594212 .   0.00271 .   0.00108 .   0.07611 .02739
.
  ** restarting optimization from step   11 **
11  -900.594366 *   0.00271 .   0.00108 .   0.04094 . .01370
14  -900.594456 .   0.00210 .   0.00083 .   0.02256 . 0.00697
15  -900.594448 *   0.00210 .   0.00087 .   0.01134 .0.00351.
16  -900.594478 *   0.00027 *  0.00011 *   0.00106 *0.00029
*

  ************************************************************
  **           Geometry optimization complete               **
  ************************************************************


        Final energy ..............  -900.59447790810

Job WF9471 completed on DIAMOND10 at Tue Nov 30 15:20:27
2004
  Reason for exit: Successful completion
  Titan Program CPU Time : 005:12:23.3
  Titan Program Wall Time: 006:57:39.8
```

6.3.3 Spartan output log file from geometry optimization of 1,3,2-diazaborolane

```
Job WF32268 started on DIAMOND10 at Tue Nov 30 18:40:52
2004
Jaguar version 3.5, release  42

  Job name:                WF32268
```

```
 Task:                    Geometry optimization

 Stoichiometry:           BC2N2H7
 Molecular weight:        70.07 amu
 Molecular charge:           0
 Spin multiplicity:          1
 Point Group:             C1

 SCF method:              B3LYP
 Basis set:               LACV3P+**
 Basis functions:           152

 Total electrons:            38
 Alpha electrons:            19
 Beta electrons:             19
 Total orbitals:            157
 Core orbitals:              19
 Open-shell orbitals:         0
 Occupied orbitals:          19
 Shells:                      1


 Non-default options chosen:
   SCF calculation type: DFT
   DFT=Becke_3_Parameter/HF+Slater+Becke88+VWN+LYP (B3LYP)
   Geometry will be optimized in redundant internal
coordinates
   Molecular symmetry not used
   Initial Hessian: from previous calculation


  Iter      Energy        Gmax        Grms        Dmax
Drms
1   -214.904414 *    0.02687 .   0.00950 .   0.17718 .   0.05001
2   -214.910376 .    0.00788 .   0.00301 .   0.17853 .   0.05000
3   -214.911344 .    0.01472 .   0.00311 .   0.16046 .   0.04637
4   -214.911822 .    0.01091 .   0.00289 .   0.04128 .   0.01467
5   -214.911815 *    0.01579 .   0.00305 .   0.04522 .   0.01530
6   -214.911968 .    0.00815 .   0.00244 .   0.02013 .   0.00731
7   -214.912240 .    0.00146 .   0.00066 .   0.01179 .   0.00402
8   -214.912266 *    0.00086 .   0.00041 .   0.01748 .   0.00602
9   -214.912301 *    0.00151 .   0.00045 .   0.05953 .   0.02097
10  -214.912374 .    0.00200 .   0.00062 .   0.01954 .0.00645
11  -214.912399 *    0.00081 .   0.00027 *   0.00556 .0.00150
12  -214.912402 *    0.00047 .   0.00013 *   0.00228 .0.00089
*
```

```
13  -214.912402 !   0.00033 *  0.00009 *  0.00246 .0.00094

  ************************************************************
  **           Geometry optimization complete               **
  ************************************************************


        Final energy ..............  -214.91240177040

Job WF32268 completed on DIAMOND10 at Wed Dec 01 02:12:05
2004
  Reason for exit: Successful completion
  Titan Program CPU Time : 004:43:10.6
  Titan Program Wall Time: 007:31:13.6
```